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THE EFFECTS OF SURFACTANTS ON THE DESORPTION
OF ORGANIC CONTAMINANTS FROM AQUIFER MATERIALS

A Dissertation
Presented to
the Graduate School of
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In Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy
Environmental Systems Engineering

by
James L. Brickell

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ABSTRACT

The efficiency of removing organic contaminants from groundwater aquifers by the pump and treat process is adversely affected by the retardation of the contaminant's mobility due to adsorption onto aquifer material. The use of surfactants in conjunction with the pump and treat process has the potential for improving contaminant mobility by solubilizing the adsorbed contaminant. (EG)

An experimental program was conducted to screen various types of commercially available nonionic and anionic surfactants for solubilizing adsorbed naphthalene from one type of aquifer material. Two additional types of aquifer materials were obtained, and the surfactant mixture, Tween 20 and Aerosol AY-65, selected during the screening process was used at various concentrations for equilibrium desorption studies to quantify surfactant effects on naphthalene desorption. Column studies subsequently were conducted to determine surfactant effects in a flow through system.

Equilibrium desorption studies showed that a 0.125 percent surfactant solution decreased the partition coefficient 65 percent compared with water alone for one soil type, while greater surfactant concentrations resulted in less effective mobilization. However, the same surfactant mixture markedly increased the partition coefficient when used with another soil type, and had negligible effects for the third soil type. It was shown that the clay mineralogy significantly influenced the effect of the surfactant solution.

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Column studies showed that mass removal efficiencies were increased by approximately 40 to 60 percent using the surfactant solution as compared with water alone. Varying flow rates did not influence the effectiveness of either the surfactant or water solutions.

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CHAPTER I

INTRODUCTION

Groundwater is the source of drinking water for about half the population of the United States. Unfortunately, contamination of some groundwater reserves has occurred, and the list of contaminated sites is increasing at an alarming rate (Hall, 1986). Once contaminated, remediation of a groundwater system is difficult and costly. One common method used for restoring contaminated aquifers is the "Pump and Treat" system. This a process in which contaminated groundwater is pumped to the surface, treated, and returned either to the groundwater system, surface waters, or other treatment facilities (Eheart, 1986; Olfenbuttel, 1984).

There has been much recent interest in the hydrogeological aspects of pump placement and pumping schemes to optimize a pump and treat system (Keely and Tsang, 1983; Lefkoff and Gorelick, 1986; Tsai and Zeilen, 1985). The costs associated with restoring a contaminated aquifer are high due primarily to the necessity of pumping and treating many pore volumes of water over a period of years to reduce the contaminant to acceptable concentration levels (MTARRI, undated; Olfenbuttel, 1984).

Proper pump placement and pumping schemes to efficiently extract the contaminated plume can reduce the volume of water that must be pumped. This volume is also affected by the physical and chemical environment of the groundwater system. For example, heterogeneities in the geological structure of the underground environment result in different flow rates. Generally, the clay rich areas which adsorb the

most contaminants have the lowest permeabilities leading to the majority of flow passing through the highly permeable areas which contain very little contaminant (MTARRI, undated).

Also, contaminant adsorption on clay and mineral particle surfaces can significantly influence aquifer remediation by retarding the movement of contaminants with groundwater. In general, the higher the extent of adsorption, the more retarded is the movement of the contaminant relative to the bulk flow of water. This decreases the concentration of the contaminant in the pumped water resulting in a larger volume of water that ultimately must be pumped to reduce the contaminant to acceptable levels.

The role of surfactants, chemical compounds that increase surface activity, in enhancing the aqueous solubility of slightly soluble substances has been known for decades. Neuberg, in 1916, extensively investigated this phenomenon, which he defined as "hydrotrophy" (Garrett, 1972). In a pump and treat process, surfactants may improve the efficiency of contaminant extraction. This could occur by increasing the solubility of the contaminant making it more mobile in the groundwater system. This, in turn, would make it easier to remove the contaminant by pumping thereby reducing the volume of water that must be pumped to remediate an aquifer. Of course, this could significantly reduce the cost of an aquifer restoration program.

This research focused on defining the equilibrium sorption effects of surfactant solutions on an organic contaminant when used in conjunction with the pump and treat process. Methods for selecting appropriate surfactants for use in this regard were identified and applied. The effects of the selected surfactant on contaminant sorption were

quantified via equilibrium sorption studies. The pump and treat process was simulated by using a flow through column apparatus.

CHAPTER II

REVIEW OF PERTINENT LITERATURE

The remediation of groundwater contaminated with organic compounds by a "pump and treat" system using surfactants involves the integration of several factors. The basic premise is that surfactants in solution can increase both the rate and extent of desorption of contaminants from aquifer material, and thereby increase the contaminant mobility to aid in its removal. Because sorption is important, background information concerning sorption processes is considered. Secondly, the nature and characteristics of surfactants are addressed, showing how and why the use of these compounds have a beneficial effect on contaminant mobility. Finally, mathematical modeling of groundwater transport is considered, along with the mobility implications of enhanced desorption.

Sorption

Sorption is the general term used to describe the process in which a chemical compound moves from one phase to be accumulated in another. The retardation of contaminant mobility caused by sorption processes is extremely important when considering the fate of a contaminant in the environment, particularly for those contaminants that are relatively persistent. Retardation due to sorption of these contaminants in a groundwater system is beneficial in that it slows the spread of a contaminant plume. However, retardation is detrimental when one attempts to remove the contaminant from a groundwater system.

Provided in this section is the background on sorption needed to understand how surfactants in solution might affect these processes.

The forces involved in the adsorption process are discussed first, followed by a brief consideration of sorption equilibria and kinetics, and factors effecting sorption processes.

Forces Involved in Adsorption Processes

Surface and Interfacial Tension

Adsorption is a surface phenomenon manifested by surface energy termed "surface tension". Neiditch (1972) defined surface tension as the work required to expand a surface by a unit area. Soluble materials can have a significant effect on surface tension. Those that decrease surface tension tend to concentrate at a surface (adsorption). Those that increase surface tension move to or remain in the bulk of solution.

Surface tension is the term used to describe surface energy when the liquid phase is exposed to air. Interfacial tension is a similar concept, but describes the excess free energies where any two surfaces come into contact. For a system where an immiscible oil is in contact with a solid and water, the amount of oil surface exposed to solid and liquid is such that the overall energy of the system is at a minimum. This situation is depicted in Figure 2.1(a). If a soluble substance is added to water which results in a decrease of interfacial tension between the solid and/or oil, the water tends to wet more of the solid and/or oil surface resulting in an increase in θ as shown in Figure 2.1(b). If the interfacial tension is reduced enough, θ reaches 180° and the oil droplet is freed from the surface of the solid (Schick, 1987). This suspension of a liquid particle within a second immiscible phase (Figure 2.1(c)) is termed "emulsification." The particle size of the dispersed phase may vary from about $0.5 \mu\text{m}$ to particles visible to the naked eye (Garrett, 1972).

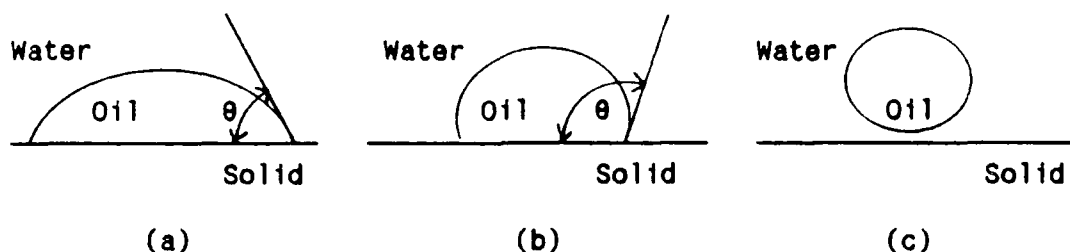


Figure 2.1 Schematic Representation of the Effects of Interfacial Tension on the Interfaces of a Solid-Oil-Water System (After Schick, 1987)

Molecular Forces

The forces that affect surface/interfacial tension may be the consequence of the hydrophobic character of the solute, the affinity the solute has for the sorbent in the system, or a combination of the two.

Hydrophobic Interactions

A solute is considered hydrophobic when water molecules show little to no affinity for the compound. Nonpolar organic compounds are typical hydrophobes because water, being a polar solvent, is essentially non-reactive towards them. A measure of this hydrophobicity is the octanol-water coefficient (K_{ow}), which is the ratio of the mass of a substance that partitions into octanol to the mass that remains in the aqueous phase in an octanol-water-solute system. The higher the octanol-water coefficient, the more hydrophobic is the solute. In general, compounds with water solubilities less than 100 mg/l and K_{ow} values greater than 10^2 are considered hydrophobic (Elzerman and Coates, 1987). These hydrophobic molecules tend to be "squeezed out" of solution, and therefore accumulate at interfaces.

Amphipathic compounds are those that have both polar and nonpolar areas (hydrophilic hydrophobe) on a single molecule. Compounds such as soaps, detergents or long chain alcohols fall into this category. In this case, the molecule orients itself such that the hydrophobic portion lies at the interface being "squeezed out" of solution, while the polar portion extends into the bulk of solution. These compounds also concentrate at interfaces like strict hydrophobes, and both types of molecules increase activity at interfaces and reduce interfacial tension (Weber, 1972). An additional characteristic of hydrophilic hydrophobes is their tendency to aggregate and form "micelles". This phenomenon is covered in detail when considering the properties of surfactants in the next major section of this review.

Solute Affinity for Sorbent

When considering the affinity solutes have for sorbents in a system, there are three basic mechanisms that must be considered: ion exchange, physical adsorption and chemisorption. In addition, two secondary mechanisms may be applicable.

Ion exchange. This is a generally reversible process in which one ion is taken from solution in exchange for another one affixed or adsorbed to a charged site on the sorbent. The ion removed from solution either has a higher affinity for the charged site on the sorbent than the ion released, or the solution concentration of the ion is significantly higher than the one adsorbed, creating a greater driving force which displaces the adsorbed ion. Bonding energies have been reported to be as high as 50 kcal/mol (Morrill et al., 1982). A charged site on the sorbent is required in this case and these charges can originate

from several different sources. Charge origination is covered in more detail under the section entitled "Factors Affecting the Adsorption Process."

Physical adsorption processes. These processes result from electrostatic interactions between ions and molecules due to electron fluctuations that produce instantaneous dipoles. The resulting attractive forces are commonly called "van der Waals" forces. These interactions are comparatively weak (1-2 kcal/mol) and decrease very rapidly as the distance between molecules increases. Van der Waals forces are operative in all adsorbate-adsorbent interactions. They are important for ions in close contact with the surface, and for nonionizable, nonpolar compounds. Molecules adsorbed due only to van der Waals forces are not fixed in position, but are free to move along the sorbent surface (Morrill et al., 1982).

Chemisorption. Chemisorption, or, chemical adsorption, occurs when the adsorbate undergoes chemical reaction with functional groups on the sorbent surface. Strong, localized chemical bonds are formed with bonding energies ranging from 30 to 190 kcal/mol. The sorbed molecules are fixed at a particular position and are not free to move along the sorbent surface. Because of the chemical reaction, this mechanism predominates at higher temperatures (Weber, 1972).

Secondary mechanisms. Included under this heading are hydrogen bonding and nonionic adsorption involving ions and groups that are attached (coordinated) to a central metallic atom of a complex. Hydrogen bonding is a partial charge transfer and is often weaker than physical

adsorption but can have bonding energies ranging from 0.5 to 15 kcal/mol. Coordination can be an important mechanism in the adsorption of nonionic polar organic compounds. Many metals present on clay surfaces can participate in coordination type bonding (Morrill et al., 1982).

One point must be emphasized: adsorption does not occur due to one distinct adsorption mechanism, but is an interaction of any number of the mechanisms discussed above. On this account, adsorption has also been classified as "specific" or "nonspecific". Specific adsorption results when charged sites of a surface exert strong forces on a particular solute, and is directly related to the number of such sites per unit surface area. Nonspecific adsorption is more general with lower heats of adsorption and is related to the interfacial area and free energy. Because of the higher energies associated with specific adsorption, nonspecific adsorption can be partially or entirely obscured as a mechanism (Morrill et al., 1982).

Sorption Equilibria

A solvent-solute-sorbent system is in a state of dynamic equilibrium when the concentration of the solute and the mass of the solute adsorbed remains essentially constant. Like all other natural phenomena, this is a thermodynamic process which occurs because the solvent, solute and sorbate attempt to achieve the lowest possible free energy state (Weber, 1972). The most common method used to describe sorption equilibrium is the sorption isotherm. Considered in this section are adsorption isotherms and hysteresis; i.e., the differences noted in the equilibrium position when a solute is being adsorbed or desorbed.

Adsorption Isotherms

An adsorption isotherm which describes partitioning of a solute between sorbent and solvent, is a plot of the mass of solute adsorbed per unit mass of sorbent versus the equilibrium solution concentration, at a specified temperature. The mathematical interpretation of sorption data led to the development of several models. Among them are the linear adsorption isotherm, Freundlich isotherm, Langmuir isotherm, Langmuir two-surface isotherm, competitive Langmuir and the Brunauer, Emmet and Teller (BET) isotherm. These models are well documented in the literature (Travis and Etnier, 1981).

Hysteresis

Hysteresis, in the context of sorption phenomenon, describes the situation where equilibrium isotherms for a system differ depending on the method used to obtain the isotherm data. When the data is taken for the case in which no solute is adsorbed on the sorbent and batch reactors are prepared with specified quantities of sorbent and solute, a particular isotherm results describing the adsorption process. However, if the sorbent is initially loaded with adsorbed solute, and data is taken for subsequent dilutions of the system where desorption occurs, a completely different isotherm may result.

Karickhoff (1984) reported that adsorption of organic materials to natural aquatic sorbents appeared to occur very rapidly, however, when desorbing, a significant portion seemed highly resistant to release. He called the portion easily desorbed, "labile", and the resistant portion, "nonlabile". He also noted a drastic decrease in the ease of extraction of sorbed solutes the longer they were incubated. This was attributed

to the possibility of an interparticle process where the solute is slowly incorporated into sorbent components. Other researchers, (Wahid and Sethunathan, 1979; Katz and Uchrin, 1986; Miller and Weber, 1986), reported similar findings concerning hysteresis.

The difference in the rates of the adsorptive and desorptive reactions (kinetics) may explain some of the apparent hysteresis effects reported in the literature. It is not uncommon for the rate of desorption reactions to be much slower than adsorption reactions (Jaffe and Ferrara, 1983). Unfortunately, researchers often arbitrarily use the same equilibration times for both adsorption and desorption isotherm determination. This practice can easily lead to a false conclusion regarding hysteresis, and emphasizes the need to ensure that equilibrium is attained when developing sorption isotherms (Lapoe, 1985).

Kinetics of Adsorption

In a groundwater system, the use of equilibrium models implies that the rate of sorption, including diffusion controlled processes, is much greater than the rate of change of the concentration of the solute by any other processes (e.g. advection, dispersion, degradation). There are circumstances, however, where the conditions of these assumptions are not met. Using soils as the sorbent material, Schwarzenbach and Westall (1981) learned from column experiments that equilibrium models were adequate as long as the velocity of the solute in the column was less than 10^{-3} cm/sec, but kinetics had to be considered for higher velocities. Karickhoff (1984) stated that true sorption equilibrium is attained only after several weeks or longer for some systems due to kinetic or steric inhibition. He attributed this to the ability of a solute to access sorbent sites, especially for large solute molecules.

Most studies of adsorption kinetics are conducted using a batch technique, wherein a series of identical samples in batch reactors is prepared. Samples are analyzed at different times after initiating the experiment, and observations of the amount of solute sorbed versus time are obtained and plotted. Most kinetic models defined in the literature describe the relationship of the data obtained in this manner.

The kinetic models most commonly used include chemical kinetic models, empirical models and the mass transfer model. When applying chemical kinetic models it is often assumed that the rate of solute sorption is related to the solute concentration and the concentration of available surface sites. Models reported in the literature include both linear and nonlinear reversible models as well as two-site models. For example (Travis and Etnier, 1981),

$$\frac{d\Gamma}{dt} = k_a(\Gamma_{\max} - \Gamma)C_t - k_d(\Gamma) \quad (2.1)$$

where

Γ = mass of compound adsorbed per gram soil ($\mu\text{g/g}$),

Γ_{\max} = ultimate compound sorption capacity of the sorbent ($\mu\text{g/g}$),

$\Gamma_{\max} - \Gamma$ = concentration of surface sites available for adsorption,

k_a = adsorption rate constant ($\text{L}/\mu\text{g}\cdot\text{h}$),

k_d = desorption rate constant ($1/\text{h}$),

C_t = solution concentration of compound in reactor ($\mu\text{g/L}$).

Integrating Equation 2.1 and applying the initial condition that none of the compound is adsorbed at time = 0 yields

$$\Gamma = \frac{k_a \Gamma_{\max} C_t}{k_a \Gamma_{\max} + k_d} \left[1 - \exp(-(k_a \Gamma_{\max} + k_d)t) \right] \quad (2.2)$$

where m is the mass of soil per liter of solution (g/L). Equation 2.1 can also be used to describe the desorption kinetics for a system that is initially at a state of sorption equilibrium, and the solution phase is subsequently diluted to affect compound desorption from the soil. Integrating Equation 2.1 and applying the initial condition that $\Gamma = \Gamma_0$ at time = 0 yields

$$\Gamma' = \frac{k_a \Gamma_{\max} C_{t0}}{k_a \Gamma_{\max} m + k_d} \left[1 - \frac{\Gamma_0 m}{C_{t0}} - \frac{f C_0}{C_{t0}} \right] \left[1 - \exp(-(k_a \Gamma_{\max} m + k_d)t) \right] \quad (2.3)$$

where

$\Gamma' = \Gamma_0 - \Gamma$, mass of the compound desorbed per gram soil ($\mu\text{g/g}$),

Γ_0 = initial amount of mass of the compound adsorbed per gram soil at the outset of the desorption experiment ($\mu\text{g/g}$),

C_{t0} = total concentration of the compound in the vial at the outset of the desorption experiment ($\mu\text{g/L}$),

C_0 = concentration of the compound in solution prior to diluting to initiate the desorption experiment ($\mu\text{g/L}$),

f = fraction of the volume of solution remaining after a portion of solution was removed to dilute each batch reactor prior to initiating the desorption experiment (unitless).

The empirical models are mathematical relationships designed to fit a curve to experimental observations, and are not strictly based on theoretical considerations. Several different models that have been reported in the literature often are used to describe the kinetics of adsorption for organic as well as inorganic materials to soils. One such model is an empirical first order model,

$$\Gamma = a(1 - e^{-kt}) \quad (2.4)$$

where

Γ = mass solute adsorbed per gram sorbent ($\mu\text{g/g}$),

t = time (h),

a = an empirical parameter representing the equilibrium sorption capacity of the sorbent ($\mu\text{g/g}$),

β = an empirical parameter related to the rate at which the system attains equilibrium ($/\text{h}$).

The empirical equation is of similar form to that of both Equations 2.2 and 2.3, where, for adsorption,

$$a = \frac{k_a \Gamma_{\max} C_t}{k_a \Gamma_{\max} m + k_d}, \quad (2.5)$$

and the rate constant,

$$\beta = k_a \Gamma_{\max} m + k_d. \quad (2.6)$$

For desorption kinetics, Equation 2.4 is used with primed values to distinguish between adsorption and desorption kinetics, or

$$\Gamma' = a'(1 - e^{-\beta' t}) \quad (2.7)$$

where

Γ' = mass of the compound desorbed per gram of sorbent,

a' = an empirical parameter representing the equilibrium desorption capacity of the sorbent,

β' = an empirical parameter related to the rate at which the system attains equilibrium.

For this case, a' is the equilibrium mass desorbed, and from Equation 2.3,

$$a' = \frac{k_a \Gamma_{\max} C_{t0}}{k_a \Gamma_{\max} m + k_d} \left[1 - \frac{\Gamma_{0m}}{C_{t0}} - \frac{f C_0}{C_{t0}} \right], \quad (2.8)$$

and β' is the rate constant.

$$\beta' = k_a \Gamma_{\max} m + k_d. \quad (2.9)$$

It is interesting to note that the rate constants for both adsorption and desorption, β and β' , are exactly the same indicating adsorption and desorption rates should be similar. Equations 2.4 and 2.7 were used to model the rates of contaminant adsorption and desorption for this study

with the relationships described by Equations 2.5, 2.6, 2.8 and 2.9 used to assist in interpreting the results of the experiments.

Lastly, the mass transfer models are most applicable when a diffusion process limits the rate of adsorption. This often occurs for porous sorbents when organic material or expandable minerals are present. A mass transport model reported in the literature (Miller and Weber, 1986) is

$$\frac{\partial \Gamma_r}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial \Gamma_r}{\partial r} \right] \quad (2.10)$$

and

$$\frac{\partial \Gamma_r}{\partial r} = \frac{k_f}{D_s \sigma_b} (C - C_s) \quad \text{at } r = R \quad (2.11)$$

where

∂ = the partial differential operator,

Γ_r = soil phase concentration of solute as a function of the radial dimension, r ,

k_f = film diffusion coefficients,

D_s = interparticle mass transfer diffusion coefficient,

σ_b = sorbent density,

C = bulk solution concentration of solute,

C_s = concentration of the solute in the liquid phase at the surface of the sorbent,

R = soil particle radius,

t = time.

Factors Affecting the Adsorption Process

The shape of an adsorption isotherm as well as the kinetic response of a system is a function of the characteristics of a specific solvent/

solute/sorbent system. Each component of this system influences the sorption process. The primary considerations for soil sorbents are whether there are organic and/or clay materials present. These factors strongly influence the amount of surface area exposed and the surface charge produced. For sorbate molecules, the chemical and physical characteristics also strongly influence the extent of adsorption. The groundwater characteristics that influence adsorption include pH, temperature, ionic strength, and the amounts and types of other solutes present.

The Nature of Soil as an Adsorbent

Soils have a large capacity for adsorbing both organic and inorganic compounds. The major components of soils responsible for adsorption are layered silicate clays, metal oxides, and organic matter. (Morrill *et al.*, 1982). The molecular composition of these components determines a soil's major physical characteristics. The complex nature of soils (i.e., a heterogeneous mixture of these components) often makes it difficult to differentiate between components affecting sorption processes.

Layered Silicate Clays

Primarily, clay minerals are crystalline aluminum or magnesium silicates with a stacked layered structure. They commonly are considered to occur in two structural types; the two-layered minerals of the kaolinite group, and the three-layered minerals which include montmorillonites, vermiculites and micas. The structural characteristics of these clays have a large impact on sorption, due primarily to the charges produced and the amount of surface area exposed.

Most clays have a net negative charge resulting from isomorphous substitution. These charges are considered the "permanent" charges.

Another type of charge produced is the "pH-dependent" charge. The primary source of this charge is considered to be the gain or loss of hydrogen ions from functional groups on the surfaces of soil solids, such as hydroxyl, carboxyl, phenolic and amine. However, these charges may also originate from damaged crystal edges.

Soil solids capable of developing pH-dependent charges include the layered silicates, oxides and hydrous oxides, as well as organic matter. At low pH, positive charge is developed and at high pH, negative charge is developed. The pH at which the sum of the positive and negative charges on the soil is zero is called the zero point of charge, ZPC (Bohn *et al.*, 1985).

The negative charge of soils is balanced by cations adsorbed to external surfaces as well as between layers for expandable clays. These cations are considered adsorbed due to electrostatic attraction and constitute the "exchangeable ions". These ions are loosely defined as those released from the soil by solutions of neutral salts. For all practical purposes, "cation exchange capacity" (CEC) is defined as the sum of the exchangeable Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} and Al^{3+} . It is clear that the amount and type of clay, the extent of isomorphous substitution, the ionizable functional groups on the soil surfaces, as well as the soil solution pH affect the CEC of the soil (Huang and Liao, 1970).

The amount of swelling of a particular clay is directly related to the amount of surface area exposed to solution. Montmorillonite and vermiculite absorb water molecules between crystal sheets causing the clay to swell. This swelling exposes more surface area to solution. As the amount of surface area exposed increases, the more favorable are the conditions for adsorption of solutes because greater surface area

provides more sorption sites, particularly for those that adsorb due to physical processes. Because kaolinite and mica do not swell, only the external surfaces are available for adsorption. Typical CECs and surface areas for some layered silicates are listed in Table 2.1.

Table 2.1 Summary of Selected Properties of Layered Silicates (Bohn et al., 1985)

Type	CEC (mmol(+)kg ⁻¹)	Surface Area (m ² g ⁻¹)	pH Dependency of Charge
Kaolinite	10-100	10-20	Extensive
Montmorillonite	800-1200	600-800	Minor
Vermiculite	1200-1500	600-800	Minor
Mica	200-400	70-120	Medium

Huang and Liao (1970) studied the adsorption of pesticides on clay minerals. They reported almost instantaneous adsorption onto kaolinite and illite (soil mica) with approximately equal capacity. However, for montmorillonite, a much higher capacity was noted along with a two-phased kinetic response. The larger capacity was a result of increased surface area due to swelling. The first phase of the kinetic response for montmorillonite was almost instantaneous adsorption similar to the kaolinite and illite, and was attributed to external adsorption. The second phase was much slower, and the authors hypothesized a diffusion-limited kinetic response because the pesticides had to diffuse to the adsorption sites between the expanded layers.

Metal Oxides and Hydroxides

The oxides and hydroxides most commonly found in soils are those of aluminum and iron. Examples are gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) in the oxide form, and $\text{Al}(\text{OH})_3$ in the hydroxide form and goethite ($\text{FeO}_3 \cdot \text{H}_2\text{O}$ or FeOOH). They are commonly referred to as amorphous gels when a noncrystalline structure is found and as oxide clays when a definite crystalline structure is present (Brady, 1984). The amorphous structure normally converts to the crystalline structure with aging.

These materials are formed by the weathering of metal silicates and often serve as cementing agents in that they tend to be found as coatings on particles in many soils. Goethite, for example, is responsible for the reddish color of soils with a high iron content (Bohn *et al.*, 1985).

Freshly precipitated hydrous oxides (amorphous material) carry a positive charge for the pH ranges typically found in groundwater, but aged oxides in many soils are negatively charged. Amorphous material is also characterized as having large surface area and is important for anion adsorption. Amorphous material accounts for most of the anion adsorption in many soils (Morrill *et al.*, 1982). The negative charge carried by oxides is much less than layered silicates, and oxides show much lower CECs than kaolinite.

Wahid and Sethunathan (1979) reported that in the absence of soil organic carbon, the iron oxide as well as clay content of the soil are important in determining the adsorption characteristics of chlorinated hydrocarbons. Lion and Garbarini (1983) found that adsorption of toluene and trichloroethene was suppressed by the presence of a hydrous aluminum oxide when organic material was present. Adsorption of these

compounds by humic acids (soil organic material) coated on aluminum oxide was enhanced when the hydrous oxide was not present. The authors hypothesized that the humic acid had a limited number of binding sites and the hydrous aluminum oxides were competing with the contaminant for these sites. They concluded that the sorption behavior of nonionic contaminants on some aquifer materials is likely to be a complex phenomena in which the nature of both the inorganic soil matrix and the soil organic matter play a role.

Soil Organic Matter

Soil organic matter is broadly classified into two groups, nonhumic and humic substances. Nonhumic substances primarily are the unaltered remains of plants, animals and microorganisms. Humic substances are the degradation products of nonhumic substances and can be further subdivided into three groups; fulvic acids, humic acids and fulvins (Morrill *et al.*, 1982).

Many researchers (Wahid and Sethunathan, 1979; Karickhoff, 1981 and 1984; Schwarzenbach and Westall, 1981; McCarty *et al.*, 1981; Schellenberg, *et al.*, 1984; Banerjee, *et al.*, 1985; Stauffer and MacIntyre, 1986) report that the total organic content of the soil (primarily the humic coating on soil particles) is the most important characteristic affecting sorption of hydrophobic organic compounds onto soil. Soil organic material controls adsorption of hydrophobic compounds when the fraction organic content (f_{oc}) is greater than approximately 0.001. Below 0.001, clays and mineral surfaces must also be taken into consideration.

Karickhoff (1984) summarized many findings of these researchers concerning the adsorption relationship between the hydrophobicity of the

solute and the organic content of the sorbent. In the case of linear sorption, the partition coefficient, K_d , can be estimated by relating it to the fraction organic content.

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2.12)$$

K_{oc} is the partition coefficient normalized to organic carbon content. This parameter has been related to the octanol/water partition coefficient through the linear model

$$\log K_{oc} = a \log K_{ow} + b \quad (2.13)$$

where K_{ow} is the octanol/water coefficient, and a and b are empirically determined coefficients for a specific solute and sorbent. Schwarzenbach and Westall (1981) found the values of a and b to be 0.72 and 0.49, respectively, for thirteen different nonpolar organic compounds and twelve different natural sorbents. Other researchers have found different values for different solutes and sorbents (Karickhoff, 1984; Bohn *et al.*, 1985; Lyman *et al.*, 1982). The basic premise of this relationship is that adsorption of hydrophobic organic material increases as the fraction organic content of the soil increases.

Thus, if the fraction organic carbon exceeds 0.001, an estimate of the amount of adsorption of hydrophobic organic material can be made by knowing the fraction organic content of the soil and the octanol/water coefficient. Below this fraction of organic carbon, the mineralogy of the soil becomes increasingly more important. It must be emphasized that use of these guidelines are for estimating purposes only. The adsorption process is a complex phenomena, and many constituents of the soil, as well as the nature of the particular sorbate and the ground-water solution, can effect this process.

The Nature of the Adsorbate

Characteristics of adsorbates that affect the rate and extent of adsorption include the composition of the adsorbate molecule along with the resulting chemical and physical characteristics. For organic compounds, factors that are important include solubility, molecular weight, size and shape of the compound; the rigidity of the molecule; the polarity of the molecule and the presence of any ionizable functional groups.

Solubility and Molecular Weight

In 1891, Traube found that for a relatively nonpolar compound and water, solubility decreases as the molecular weight of the compound increases (Traube's Rule). The general relationship between adsorption and solubility was first presented by Lindelius in 1920. "Lindelius' Rule", states that the more soluble a substance is, the less it will be adsorbed (Lapoe, 1985).

These general rules are not always applicable, however, as Lapoe (1985) reported. Morrill *et al.* (1982) gave several hypotheses why this may be so. In some cases, adsorption may decrease as molecular size increases due to the formation of aggregates (micelles) which may become more soluble in the aggregated state. Another possibility is that large molecules may polymerize and cause clay particles to aggregate. This could have the effect of reducing the soil's effective surface area and binding sites.

Size, Shape and Structural Rigidity of the Adsorbate Molecule

In addition to the effect size has on solubility and polymer formation, it is also important in steric considerations in the sorption

process. Shape and rigidity can be factors concerning the ability of a molecule to reach an adsorption site as well its ability to align properly for adsorption. When diffusion is important, such as between clay unit layers or porous organic material, the size, shape and structural rigidity of the sorbate molecule may determine the rate and extent of sorption.

Polarity and the Presence of Ionizable Functional Groups

Karickhoff (1984) stated that nonhydrophobic interactions contribute to or dominate sorption in some instances. This tends to occur in coincidence with one or both of the following conditions: (1) high sorbate polarity or highly polar or ionizable functional groups conducive to site specific bonding with polar groups or charged sites on sorbent surfaces; and (2) low organic content in the sorbent, especially when there is also a high clay content.

Low polarity aliphatic hydrocarbon sorbates are poor competitors with water for charged adsorption sites. When these compounds adsorb to clay minerals, they do so predominately on external surfaces due to van der Waals forces. Lapoe (1985) reported little sorption of chlorinated aliphatic hydrocarbons on a variety of pure clays and minerals. For natural soils he found a strong correlation between sorption distribution coefficients (K_d) and the polarizability of chlorinated aliphatic molecules. In fact, he found this correlation to be stronger than one relating sorption and the fraction organic carbon content of the soil. The relationship showed an increase in adsorption as the polarizability of the molecule increased.

Aromatic hydrocarbons such as benzene and naphthalene tend to adsorb to a larger extent than aliphatics. This is because its pi orbital

electrons have a high electron density giving the molecule the capability of interacting with cations affixed to clay. Organic coatings on clay material also are important factors in contaminant sorption. The primary interaction is between the contaminant and functional groups of the organic coatings. Alcohols, ketones, aldehydes, ethers, acids, nitriles, amines, organophosphates, and organosulfur compounds all have been shown to influence adsorption to both organic and mineral sorbents (Morrill *et al.*, 1982).

The Nature of the Groundwater Solution

Factors of importance in this section are the pH of the soil solution, ionic strength, and the presence of other solutes. Although temperature variations might also be considered, they are not of sufficient magnitude in groundwaters to have much of an effect on sorption.

Dependence on pH

Weber (1972) stated that, in general, adsorption of organic material decreases as pH increases. Stauffer and MacIntyre (1986) found this to be the case for low polarity organic compounds on several minerals and aquifer materials. Talbert and Fletchall (1965) also reported decreased adsorption of pesticides on kaolinite, illite and montmorillonite as pH increased.

The pH of groundwater is a function of the composition of the aquifer and the chemical and biological processes occurring during infiltration. Generally, pH is in the range of 6 to 9 (Stumm and Morgan, 1981). Lapoe (1985) found negligible effects on the sorption of trichloroethene on mineral soils over the pH ranges normally found in groundwater. In contrast to Weber's (1972) generalization of decreased sorption as pH

increases, however, Lapoe (1985) reported that increasing pH may have the effect of reducing the solubility of certain organic components such as humic acid, resulting in increased adsorption to the solid phase, particularly for soils with high fractions of organic carbon. In addition, changes in pH can affect interfacial tensions, particularly when there are surfactants in solution (GAF, 1982), resulting in changes in the sorption characteristics of the system.

Effect of Ionic Strength and Other Solutes

For site specific competitive sorption, inorganic ions often are directly involved in the sorption process. For most neutral sorbates, the most important effect of ionic strength is on the aqueous phase activity coefficient. Although the partition coefficient can remain constant, vary directly or vary inversely with ionic strength, an increase in hydrophobic sorption with increased ionic strength is more typical, but usually not significant (Karickhoff, 1984).

The soil solution is a mixture of many compounds and can contain many or few inorganic and organic constituents. The compounds may mutually enhance adsorption, may act relatively independently or interfere with one another. The actual effect often depends on how the groundwater constituents affect speciation of a particular contaminant. For example, dissolved organic matter (DOM) or cosolvents present in the soil solution generally decrease adsorption by forming soluble complexes with organic contaminants (Caron et al., 1985; Carter and Suffet, 1982; Chiou et al., 1986; Karickhoff, 1984; Garret, 1972, Fu and Luthy, 1986; Nkdel-kizza et al.; Slöblom and Söderlund, 1985). Organic contaminants may remain associated with soluble DOM, and if the DOM does not adsorb,

neither does the particular contaminant. Other transformations that may effect the speciation of a contaminant include the effects of hydrolysis, substitution and elimination reactions, oxidation and reduction reactions, biological transformations, volatilization and precipitation reactions (Mabey and Mills, 1986).

Surfactants

The word "surfactant" is a shortened form of the term "surface active agent." The outstanding property of these compounds is that they tend to concentrate at interfaces of aqueous solutions altering the surface properties. A characteristic feature of a surfactant is the presence of strongly hydrophilic and hydrophobic groups linked in a single molecule. The hydrophilic group is soluble in water while the hydrophobic group is squeezed out, resulting in a higher concentration at surfaces than in the bulk of solution. This effect results in a lowering of surface tension with a possible consequence of emulsifying immiscible liquids or suspending solid materials.

When surfactant molecules aggregate in solution, micelles are formed with the hydrophobic portion of the molecule oriented towards the middle of the aggregate. These soluble aggregates can result in the solubilization of certain hydrophobic organic compounds by providing a nonpolar environment in which the hydrophobic compound can partition. This phenomenon is important in the context of this project.

The information required to relate how the addition of surfactants to contaminated groundwaters can affect the sorption of contaminants is detailed in this section. Background information reviewing the structure of various surfactants available is provided first. This is

followed by a discussion of the commercial uses of surfactants with an emphasis on the area of focus most applicable to this study; enhanced oil recovery. Surfactant use and research for soil and groundwater decontamination are also discussed. Finally, the characteristics of surfactants that aid in determining the most appropriate classes and types for use in this investigation are explored.

Background

The basic structure of a surfactant involves a single molecule containing both a strongly hydrophilic and a strongly hydrophobic portion (i.e., a "hydrophilic hydrophobe"). Some of the sources for both the hydrophobic and hydrophilic groups are listed in Table 2.2.

Table 2.2. Hydrophobic and Hydrophilic Groups Commonly Found in Surfactant Molecules (Extracted from Swisher, 1987)

Hydrophobic	Hydrophilic
Fatty acids	Sulfonate
Paraffins	Sulfate
Olefins	Carboxylate
Alkylbenzenes	Quaternary ammonium
Long chain alcohols	Protonated amine
Alkyl Phenols	Sucrose
Polyoxypropylenes	Polypeptides
	Polyoxyethylene

When a hydrophobe and hydrophile are associated to form a surfactant molecule, the type of hydrophile is used to classify the surfactant. The general classifications include anionic, nonionic, cationic and zwitterionic. For anionic surfactants, the hydrophile ionizes to

form an anion consisting of either of the first three hydrophilic groups listed in Table 2.2. Cationic surfactants generally are considered the quaternary ammonium or protonated amino compounds. James (1987) indicated that in practice, only the cationic compounds in which the positive charge resides on a nitrogen atom contained in either a protonated amino or quaternary ammonium compound are of commercial significance. Other cationic surfactants either are too toxic or too expensive. Sucrose, polypeptides and polyoxyethylene, are common nonionic surfactant hydrophiles. The zwitterionics are amphoteric with both anionic and cationic centers on each molecule. These surfactants are expensive and are produced only in relatively small quantities for specialty purposes. Common surfactants formed from the list of hydrophobes and hydrophiles of Table 2.2 are summarized in Table 2.3. Only several of the literally hundreds of surfactants commercially available are listed.

Commercial Uses of Surfactants

The most common use of surfactants, as far as the general public is concerned, is in the use of detergents. "Detergent" is a term usually used to describe a formulated product. A commercial detergent may contain, in addition to a surfactant, such materials as builders, suds controlling agents, soil suspending or anti-redeposition agents, anti-corrosion agents, fabric whiteners, bluing agents, bleaches, fabric softeners, antibacterial agents, perfumes and others (Neiditch, 1972).

Surfactants, however, also find numerous industrial applications. Karsa (1987) reviewed twelve industrial sectors that make extensive use of surfactants. All of the industries listed in Table 2.4 exploit a surfactant's ability to emulsify, suspend or solubilize compounds of

Table 2.3. Typical Anionic, Nonionic and Cationic Surfactants (Extracted from Swisher, 1987)

ANIONIC

Alkylbenzenesulfonates (ABS)
Alkane sulfonates
Olefin sulfonates
Ester and amide sulfonates
Sulfo fatty acids
Sulfosuccinate esters
Primary alkyl sulfates
Secondary alkyl sulfates

NONIONIC

Alcohol ethoxylates
Alkylphenol ethoxylates
Polyoxyethylene esters
Polyoxyethylene-polypropylene derivatives

CATIONIC

Alkyl trimethylammonium
Alkylbenzyl dimethylammonium
Dialkyl dimethylammonium
Alkyl pyridinium
Alkyl imidazolinium
Alkylamine

concern into a variety of solvents. The industry having the closest relationship to the process of removing organic contaminants from aquifer soils, with the highest likelihood of technology transfer, is the petroleum and oil industry. This is particularly true in the case of enhanced oil recovery efforts.

Table 2.4. Industrial Applications of Surfactants (Karsa, 1987)

Textiles and fibers	Paints, lacquers and inks
Mineral extraction and processing	Food industry
Pulp and paper	Agriculture
Leather and fur	Petroleum and Oil
Civil engineering	Plastics, rubbers and resins
Industrial and institutional cleaning	Metal and engineering

Enhanced Oil Recovery

Primary oil recovery is accomplished through the natural pressure of volatile components in an oil reservoir. As oil is removed from the reservoir, this natural pressure is depleted, and secondary oil recovery is often employed. This involves the injection of water and steam into the reservoir to increase the pressure and remove more of the trapped oil. Even after secondary oil recovery, approximately 60% of the oil remains in the reservoir, clinging to reservoir solids. This oil is the target for tertiary, or "enhanced" oil recovery (Ling et al., 1987).

The Enhanced Oil Recovery (EOR) Process

A typical EOR process often involves injecting three slugs of water with different chemical compositions. The first slug, an aqueous solution of sodium chloride, is applied for two purposes. The first is to

screen the surfactant slug from the reservoir brine, and the second is to exchange cations in the reservoir solids, replacing magnesium and calcium with sodium. Removal of the divalent ions reduces the potential for precipitating the surfactant with calcium or magnesium. The trailing portion of this first slug contains other inorganic salts to reduce surfactant adsorption. The surfactant slug which follows reduces the interfacial tension between the oil and water. The third slug contains a mobility control agent composed of water soluble biopolymers designed to drive the mobilized oil to producing wells (Foster, 1973).

Many considerations are necessary to design an efficient enhanced oil recovery process. The major parameters that affect the process include very low surface tensions and wettability at the rock-fluid interface (Ling et al., 1987). Lucassen-Reynders (1981) related that interfacial tensions on the order of 10^{-2} to 10^{-4} dynes/cm have been achieved for surfactant formulations based on petroleum sulfonates combined with a cosurfactant or a cosolvent. These ultralow surface tensions are necessary to efficiently emulsify crude oil removing it from the reservoir solids. Hill et al. (1973) reported that properly constituted aqueous systems containing less than 1.0% by weight petroleum sulfonates yield interfacial tensions with crude oil below 2×10^{-4} dynes/cm. These have been noted to displace discontinuous oil from sandstone cores. Petroleum sulfonates are unidentified complex mixtures. It is generally agreed that ultralow tensions can only be attained using mixtures of surfactants (Lucassen-Reynders, 1981).

As the interfacial tension between the water and the minerals in the underground oil reserve is decreased, the adhesive forces between the water and the mineral surfaces are increased. This not only has the

effect of aiding the removal of oil from solid surfaces, but also keeps oil from re-entrapment. It is clear, therefore, that the interfacial tension between the oil and aqueous phases as well as the aqueous and solid phases are important considerations when evaluating the appropriateness of a specific surfactant slug composition.

Results of EOR Investigations

The petroleum industry has done extensive research into the EOR process. Although much of this work is proprietary, much has also appeared in the literature. Some results that may be applicable to groundwater decontamination are reviewed below.

Shaw (1984) investigated oil recovery in sandstone cores using a 10 percent pore volume surfactant slug containing 3.0 percent sodium iso-stearate and 3.0 percent isopentyl alcohol followed by a polyacrylamide mobility buffer. He reported 92 percent tertiary oil recovery. Ling et al. (1987) explained possible effects of alcohol addition to the surfactant slug. Among the possibilities listed are the lowering of interfacial tensions and reducing the interfacial viscosity. Hill (1973) found that oil recovery efficiency is improved by adding sodium tripolyphosphate. This is due to its compatibility with multivalent cations as well as a reduction in the adsorption of sulfonates on the sandstone surfaces.

Bernard (1975) investigated the effect of clays, limestone and gypsum on the EOR process. He found that clay and gypsum greatly reduced the oil recovery efficiency of the soluble oil-polymer flood, while limestone had essentially no effect. Also, the effect of clay on the process is influenced significantly by the salinity of the aqueous

solution. When the salinity was low, clay greatly reduced oil recovery efficiency, and when salinity was high, clays had only a moderate effect on efficiency. Bernard (1975) related that the reduction in efficiency is due to surfactant and polymer adsorption on the clay.

The possibility of technology transfer from enhanced oil recovery processes to groundwater decontamination efforts exist; however, the limitations must be recognized. Enhanced oil recovery processes involve the removal of hydrocarbons existing as a separate liquid phase, and a removal efficiency of approximately ninety percent would be considered excellent. Groundwater decontamination objectives, however, require much greater removal efficiencies. In most cases the crude oil remaining after the process is terminated is the most difficult to recover. This unrecovered oil would be representative of the contamination targeted by groundwater decontamination efforts. Also, many groundwater remediation efforts involve soluble contaminants rather than those existing as a separate immiscible phase.

Decontamination of Surface Soils Using Surfactant Solutions

Gaynor and Volk (1976) investigated the effects of anionic (sodium olefin dodecylbenzene sulfonate), nonionic (isooctyl phenyl polyoxy-ethanol) and cationic (cetyl pyridinium chloride) surfactants on the adsorption of the pesticide picloram (4-amino-3,5,6-trichloropicolinic acid) on soils. They attempted to correlate their results with selected soil properties, including organic matter, clay content, extractable aluminum, cation exchange capacity and pH. The fraction of organic matter in the soils they used ranged from 0.7 to 7.7 percent. Their results showed:

1. Freundlich K values correlated with extractable aluminum and clay content.
2. Picloram adsorption from aqueous, nonionic and anionic solutions was greater at pH 5 than at pH 7.
3. The anionic surfactant competed with picloram for adsorption sites on the soils at pH 5.
4. Picloram adsorbed to soils from solutions containing 0.1 and 1.0 percent cationic surfactant to a greater extent than it did from aqueous, anionic or nonionic solutions.
5. When using a 10 percent cationic surfactant solution, picloram adsorption was similar on soils at pH 5 and 7 and increased with decreased organic content.
6. In many cases, a 1.0 percent concentration of an anionic surfactant decreased picloram adsorption, while a 10.0 percent concentration increased the extent of picloram adsorption.
7. Depending on the soil type, nonionic surfactants either increased or decreased picloram adsorption.

The focus of this report primarily was to investigate the use of surfactants for mobilizing a pesticide, thereby making it less persistent in the environment. The objective of mobilizing a contaminant for removal with a pump and treat remediation project is similar, and the results reported may be useful for comparing with the results of this study.

The U.S. Environmental Protection Agency has an ongoing Chemical Countermeasures Program to evaluate in-situ methods for mitigating environmental damage from hazardous material contamination of surface soils. As part of this program, investigations were made to assess the effectiveness of employing aqueous surfactants to aid in the cleanup of contaminated soils using standard water washing techniques. These investigations involved laboratory studies as well as a field study at a site of opportunity.

The laboratory investigations (Ellis et al., 1985) involved batch equilibrium and column studies to remove contaminants from a surface

soil that was representative of "Superfund" sites. The contaminants included intermediate and high molecular weight aliphatic hydrocarbons and polynuclear aromatic hydrocarbons, a polychlorinated biphenyl (PCB) mixture in chlorobenzenes, and di-, tri-, and pentachlorophenols.

Initially, a surfactant solution of 2.0 percent Richonate YLA (anionic) and 2.0 percent Hyonic NP-90 (nonionic) was used based on a Texas Research Institute study concerning the removal of gasoline from sand particles. This combination was found to be unsuitable because of the mixture's tendency to suspend clay and silt size particles which resettled in small pores and inhibited flow. Several surfactants and surfactant combinations were tested for the following characteristics: adequate water solubility, low clay particle dispersion, good oil dispersion and adequate biodegradability. The surfactants selected for the study were Adsee 799 and Hyonic NP-90, both nonionic surfactants. The optimum concentration was found to be 1.5 percent total, with each surfactant comprising 0.75 percent. For the batch equilibrium studies this solution resulted in a 93.0 percent removal efficiency for hydrocarbons and 98.0 percent for PCBs.

In the soil column studies, very limited removal of aliphatic hydrocarbons occurred using water alone, even after 10 pore volumes. After the passage of three pore volumes of aqueous surfactant, however, the soil material was significantly cleaner, and after 10 pore volumes, the soil was effectively decontaminated. All aromatic hydrocarbons had been completely removed after the third pore volume of aqueous surfactant had been applied.

Because the results of the laboratory study showed that the use of surfactant solutions was effective in decontaminating soils, a site of

opportunity was located to field test the process. The site was heavily contaminated with jet fuel, chlorinated solvents and fire fighting foams. Leaching experiments were carried out using a 1.5 percent blend of Richonate YLA and Hyonic NP-90. The treatment results were good, with a 90 percent reduction in hydrocarbon levels. Although soil clean-up was good, problems existed regarding treatment of the leachate generated. (McNabb et al., 1985; Nash and Traver, undated)

Another process investigated by the EPA was the extraction, treatment, and redeposition of contaminated surface soils. A mobile system was developed consisting of two major soil scrubbing components; a water-knife stripping and soaking unit for disintegrating the soil matrix and solubilizing the contaminant from larger particles and a four stage countercurrent extractor for freeing the contaminants from smaller particles.

Tests were run to determine what cleaning water additives would increase the efficiency of the system. Nonionic surfactants, TWEEN 80 (a polyoxyethylene sorbitan fatty acid ester) and MYRJ 52 (a polyoxyethylene acid), were tested. For inorganic soils, water alone showed a 24.6 percent removal of PCBs. This increased to 37.5 percent when a one percent solution of TWEEN 80 was used. For organic soils, water alone removed 48.3 percent of the PCBs, while a one percent solution of TWEEN 80 removed only 23.8 percent (Scholz et al., 1983).

Additional testing was performed subsequently to investigate the use of a commercially available industrial strength detergent (Traver, 1986). This resulted basically in a washing of the fine particles from the soil matrix. Since the vast majority of the contaminants were attached to the fine particles, the larger particles could be returned

to the site. The contaminated fines, however, had to be disposed of by conventional methods (e.g., landfill, incineration).

Rickabaugh et al. (1987) conducted laboratory scale studies to examine the effectiveness of aqueous surfactant solutions for decontaminating soil from a hazardous waste site. The soil contained 2078 mg/kg of chlorinated hydrocarbons. Batch studies were performed using fourteen commercially available surfactants; four anionic, eight nonionic, one cationic and one nonionic/anionic blend. Experimental results obtained from tests in which surfactant concentrations of 0.5, 1.0 and 2.0 percent were utilized showed that removal of chlorinated hydrocarbons increased as the concentration of the surfactant increased. Among the different surfactants tested, a nonionic surfactant (ethoxylated nonylphenol) showed the best total chlorinated hydrocarbon removal (150 mg/kg). Two surfactants, an anionic (phosphated alkyl ethylene oxide) and nonionic (polyethylene oxide alcohol), had similar removal rates (135 mg/kg).

Column studies were performed subsequently using the surfactants tested in the batch studies as well as mixtures of those surfactants. Total surfactant concentration was 2.0 percent. A nonionic/cationic blend proved to provide the best removal (59 percent) followed by a single nonionic surfactant (55 percent). The next two most effective were mixtures of anionic/nonionic surfactants (51 and 46 percent). For the same scrubbing time, water alone removed less than 1.0 percent of the contaminants.

The studies described above all dealt with the decontamination of surface soils. The objective of remediating both surface soils and groundwater aquifers is the same; to remove contaminants. However,

conditions under which this objective is pursued can be significantly different. Contaminated surface soils generally contain more organic material and exist in unsaturated conditions. In contrast, saturated conditions exist in groundwater aquifers. Also, the mineralogical characteristics of aquifer material can differ markedly from surface soils. Finally, because an aquifer is a conduit for groundwater flow, the surfactant effects on permeability is of greater concern than for surface soils.

Groundwater Decontamination Using Surfactant Solutions

MTA Remedial Resources, Inc. (MTARRI), developed an aquifer restoration procedure utilizing technology transfer from the petroleum industry's enhanced oil recovery research. The process involves the use of alkaline agents, polymers and surfactants. The target contaminants are aromatic, aliphatic and/or chlorinated organic compounds. MTARRI claims that the costs for remediating a contaminated aquifer can be reduced by 50-80 percent using this system.

A preflush of 0.1-1.0 percent concentration potassium hydroxide, sodium hydroxide, or sodium silicate is used at the outset. MTARRI related that the sodium or potassium adsorbs onto the clay surfaces displacing the adsorbed organic contaminants. A 0.1-1.0 percent solution of sulfonate then is added washing the contaminants from the mineral grains and retaining the contaminants in solution. To minimize the confounding effects of heterogeneous permeability within an aquifer, a polymer can be employed to direct the surfactant solution to zones of low permeability (MTARRI, undated). In the EOR process, the mobility control slug is applied last to push the surfactant slug through the oil

bearing reserve. In contrast, MIARRI uses the mobility control slug before, or simultaneously with, the surfactant slug. Mobility control is accomplished by reducing the pore size in zones of high permeability, forcing the subsequent surfactant slug through the clay zones where more contaminants are likely to be adsorbed.

Surfactant Characteristics

Most of the characteristics surfactants exhibit depend upon the structure and type of surfactant molecule. One of the most important features is that of micelle formation. Following a discussion of this topic is a discussion of the characteristics of organic and particulate dispersion, solubility, adsorption, biodegradability and toxicity.

For purposes of the present investigation, desirable surfactant characteristics concerning dispersive properties are good organic dispersion and minimal effect on particulate dispersion; i.e., the organic contaminant must be mobilized while the soil matrix is left intact. Also, the surfactant must be sufficiently soluble to perform its intended function, and should remain in solution and not adsorb to soil matrix. Since surfactants are intended for use in a groundwater system, a reasonable rate of biodegradability as well as minimal toxicity are important criteria.

Micelles

When a surfactant is dissolved in water at a low concentration and the concentration subsequently is increased, a dramatic change in several physical properties of the solution occurs. Properties such as surface tension, conductance, vapor pressure, turbidity and the solubility of compounds that normally are sparingly soluble in water change sharply

over a relatively narrow range of surfactant concentrations (Hall and Tiddy, 1981). Only the monomer form of the surfactant is present at low concentrations, and the change in physical properties occurs when monomers begin to aggregate. The aggregates are called micelles, and the concentration (actually, a value representing the range) at which aggregates form is called the critical micelle concentration (CMC). Nearly all surfactant added above this concentration form micelles.

Micelle formation is a thermodynamic process, and formation of micelles from the constituent monomers involves a rapid, dynamic association-dissociation equilibrium (Mukerjee and Mysels, 1971). Micelles are thermodynamically favored when their formation results in minimizing the free energy of the system. This occurs through the heat released during micelle formation and the increase in entropy attributed to a disruption in the structure of water (Hall and Tiddy, 1981).

Micelles are arranged in solution with the hydrophobic portions of the surfactant molecules oriented toward one another, while the hydrophilic portions are associated with water molecules. The interior of a micelle closely resembles a liquid hydrocarbon. A typical micelle is shown in Figure 2.2.

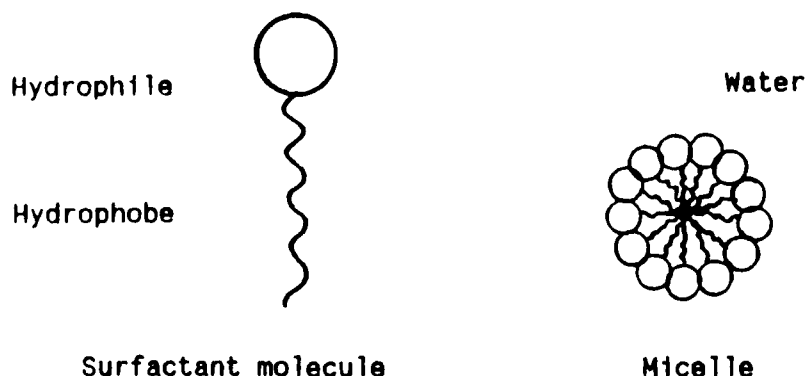


Figure 2.2. Typical Surfactant Molecule and Micelle

It is interesting to note that although micelles are made up of surface active molecules, the micelle itself is very soluble and not surface active. Consequently, when a slightly soluble organic contaminant partitions into a soluble micelle, the solution concentration of the contaminant increases and there is an apparent increase in the contaminant's solubility. The phenomenon is called "solubilization" and the compound solubilized is the "solubilize." Solubilization may be regarded as the formation of mixed micelles by surfactants and substances which do not themselves form micelles. Solubilization is a partitioning process, in this case between micellar and aqueous phases, with

$$K_m = \frac{\text{Amount solubilized per micellar molecule}}{\text{Concentration of unmicellized solubilize}} \quad (2.14)$$

where K_m is defined as the partition coefficient. Values of K_m are on the order of 10^3 to 10^4 when concentrations are expressed as mole fractions. As might be expected, these values increase with increased hydrophobicity of the solubilize (Hall and Tiddy, 1981).

Schick (1987) reported that the solubilizing effect of micellar solutions is an important mechanism for oil removal from a solid surface. Since micelle formation must occur in order for solubilization to take place, factors influencing the CMC are important. Characteristics of the surfactant as well as the aqueous system must be considered. These include the types and structures of the surfactant's hydrophilic and hydrophobic groups, the ionic strength and temperature of the aqueous solution as well as the effects of surfactant mixtures.

Effects of Surfactant Structure on Micelle Formation

The structure of both the hydrophilic and hydrophobic portions of the surfactant molecule influences the CMC. For a given hydrophobe, nonionic surfactants have lower CMCs than ionic surfactants (Hall and Tiddy, 1981). Attwood and Florence (1983) attribute the lower CMC's for nonionic surfactants to less electrical work required in micelle formation. For the polyoxyethylene nonionic surfactants, the smaller the number of ethylene oxide groups, the lower is the CMC (Chiu *et al.*, 1984).

For monovalent ionic surfactants, CMC values do not depend strongly on the nature of the charged group, but a charged group increases the CMC by two or three orders of magnitude over an uncharged group. Divalent counterions lead to lower CMCs than monovalent ions (Hall and Tiddy, 1981).

The structure of the hydrophobic group has a drastic effect on the CMC. The CMCs of the various homologs of surfactants with a linear alkyl chain follow the equation

$$\log \text{CMC} = A - Bn_1 \quad (2.15)$$

where n_1 is the alkyl chain length and A and B are constants. This equation has values for B in the range of 0.29 to 0.50. It is clear, therefore, that the CMC decreases as alkyl chain length increases.

Several other structural characteristics of the hydrophobic chain affect the CMC. Benzene rings have the same effect as adding 3.5 CH₂ groups to the chain. Branching as well as unsaturation of the hydrophobic chain also increases the CMC (Garrett, 1972; Hall and Tiddy, 1981).

Effects of Ionic Strength and Temperature on Micelle Formation

For ionic surfactants, the addition of an electrolyte lowers the CMC. For a common counterion (i.e., one of the ions resulting from the addition of an electrolyte is the same as one formed by the addition of the surfactant), the reduction may be described by

$$\log m_1 + \beta \log m_2 = K_1 \quad (2.16)$$

where m_1 and m_2 are the total concentrations of surfactant ions and counterions at the CMC and K_1 is a constant. For univalent surfactants, β is on the order of 0.6 to 0.7 when the counterions are monovalent, and about half those values when the counterion is divalent. Electrolytes also lower the CMC of nonionic surfactants, but the effects are much smaller than for ionics. For the nonionic surfactant, NP(EO)₁₀ (nonyl-phenol polyethoxylate with an average of 10 ethylene oxide groups per molecule), Stellner and Scamehorn (1986) showed a decrease in the CMC from 53 $\mu\text{mol/L}$ at a zero concentration of Na^+ , to 27 $\mu\text{mol/L}$ with a 1.2 molar solution of Na^+ . The anionic surfactant, sodium dodecyl sulfate (SDS), under similar Na^+ concentrations, however, showed a decrease in the CMC from over 3000 to under 200 $\mu\text{mol/L}$.

Temperature also has an effect on the CMC of a surfactant solution. However, the effects are generally small and complex, with curves of CMC versus temperature frequently exhibiting a minimum (Hall and Tiddy, 1981).

Effects of Surfactant Mixtures on Micelle Formation

Cox *et al.* (1985) showed that when a nonionic surfactant with the hydrophobic portion of the molecule containing twelve CH_2 groups and the

hydrophilic portion consisting of polyethylene oxide is added to linear alkane sulfonate (LAS, an anionic surfactant) the CMC is significantly lowered and the micelles that were formed predominately consisted of nonionic molecules. They reported that the nonionic surfactant acts as a micelle promoting agent while the LAS remained responsible for surface and interfacial properties. In addition to lowering the CMC, this mixture was highly resistant to the precipitation of LAS by Ca^{2+} . Their laboratory study showed best performance when the nonionic surfactant had linear hydrophobic chains containing 10 and 12 carbon atoms, and the hydrophilic portion had 70-80 percent ethylene oxide content. Stellner and Scamehorn (1986) also showed a much reduced CMC for the mixture of NP(EO)₁₀ and SDS.

Organic and Particulate Dispersion

Organic contaminant dispersion occurs principally due to the mechanisms of solubilization and emulsification. Solubilization, a function of micelle formation, was discussed in the previous section. Most of the data concerning these properties of surfactants derive from the detergent industries. Their primary focus is to relate the removal of oil and particulate soil from cloth fibers.

Schick (1986) presented data concerning the deposition of stearic acid (considered a "fatty soil") on polymer fibers. A nonionic surfactant, polyoxyethylene (9) nonylphenol, was very effective at inhibiting deposition of stearic acid on the polymer at concentrations above the CMC. Below the CMC, though, the surfactant had little effect. In contrast, an anionic surfactant, SDS, was moderately effective in reducing deposition at concentrations above the CMC. Below the CMC, deposition

actually increased when using SDS. The author concluded that nonionic surfactants used at concentrations above the CMC are superior in laundering synthetic fabrics in the presence of oily soil.

For clay removal from fibers, Schick (1986) found that nonionic surfactants are more effective. Polyoxyalkylated compounds showed the most effective removal of montmorillonite from cotton fibers. The author postulated that polyoxyethylene compounds are strongly adsorbed by montmorillonite and they remove the top two or three layers due to their capacity to intercalate between unit layers, breaking up their stacks. These nonionic surfactants are considered anti-redeposition agents, as they cause little or no flocculation of clay slurries. Sutton's (1987) report contradicts Schick somewhat. He states that it is generally true that alkylbenzene sulfonates (ABS, an anionic surfactant) show optimal performance against particulate soil, whereas nonionics perform better on oily soils.

Solubility of Surfactants

The principal role of the hydrophilic portion of the surfactant molecule is to give the hydrophobic carbon chain sufficient solubility that the CMC values can be reached or exceeded (Mukerjee, 1971). In general, the longer the hydrophobic chain, the lower is the solubility. If the CMC can be reached, the apparent solubility is very high as the micelles formed are very soluble (Garrett, 1972). For anionic surfactants, the optimal chain length for solubility is ten to twelve carbons (Sutton, 1987). For nonionics, water solubility increases with an increasing number of ethylene oxide groups (Cox, 1986). Although Traube's general rule of solubility decreasing with increased molecular weight

may apply on occasion, in most cases surfactant molecules are too polar for this rule to be applicable.

For anionic surfactants, the presence of Ca^{2+} ions reduces solubility due to precipitation. As previously mentioned, mixing nonionic surfactants with anionics can reduce this effect. Also, addition of sequesterants such as sodium triphosphate reduces precipitation of calcium-surfactant molecules (Schwuger, 1981). Temperature has the same general effect on surfactant solubility as it does with most other solids or liquids; solubility increases with increases in temperature (Hall and Tiddy, 1981).

Adsorption of Surfactants

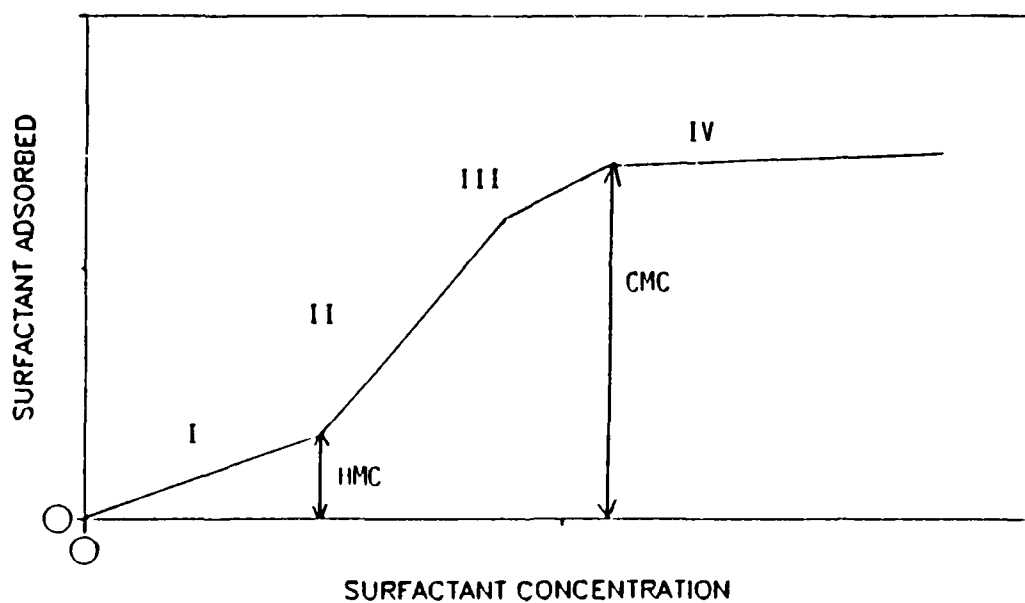
It is well known that surfactants concentrate at interfaces. This is necessary to reduce interfacial tension to emulsify oils. In the context of this study, however, it must be recognized that a distinct hydrocarbon liquid phase is not present, and that retardation of the contaminant is due to adsorption of the organic contaminant on the aquifer material. This results in contaminant solution concentrations on the order of micrograms or milligrams per liter, not in a distinct liquid hydrocarbon phase. Consequently, a desirable characteristic of a surfactant is to keep as much of it in the micellar stage in order to solubilize organic contaminants. This means that adsorption of the surfactant should be minimal. Unfortunately, the characteristics of surfactants that make them good micelle formers also are the characteristics causing them to adsorb.

Structural variations in the sulfonate surfactants are found to produce specific adsorption effects (Somasundaran et al., 1984)

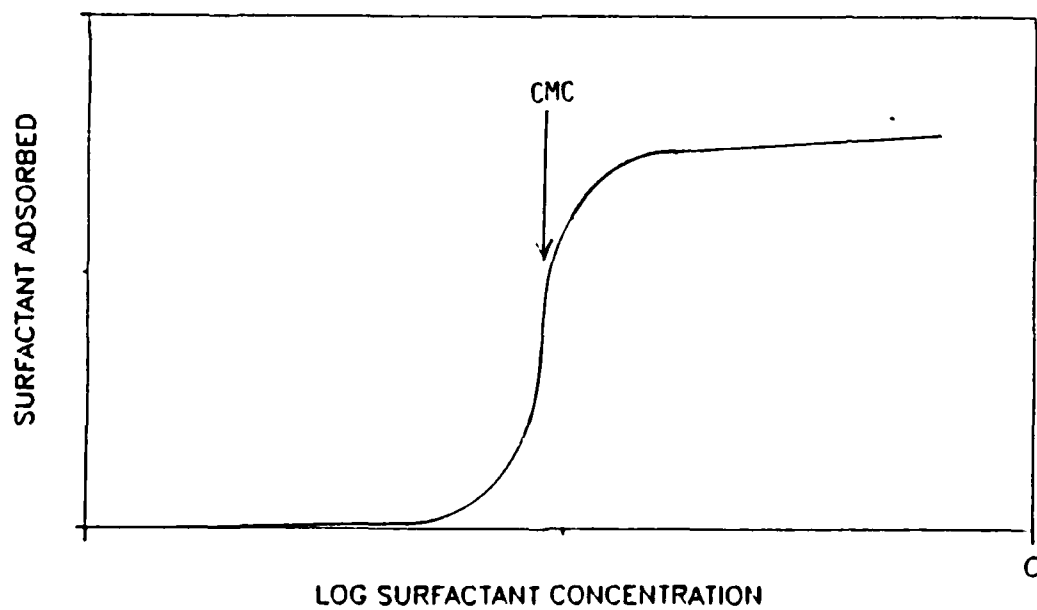
including: an increase in the chain length of the alkyl group increases the adsorption of these compounds except when in the micellar region; the presence of alkyl substitutes on alkylarylsulfonates decreases adsorption; and branching (the more branching, the less adsorption) and position of phenyl groups on the hydrophobic chain affects the extent of adsorption.

Lopata *et al.* (1988) presented a typical anionic adsorption isotherm on a positively charged mineral oxide surface showing four distinct regions (Figure 2.3). Region I which includes the lowest surfactant concentrations, exhibits linear sorption and is termed the "Henry's Law" region. Surfactant molecules adsorb primarily due to electrostatic attraction between the surfactant head groups and the oppositely charged surface. The hydrophobic portion of the molecule, however, also plays a role in that it interacts with the surface causing the entire molecule to lie essentially flat against the soil surface. At a certain concentration, adsorption is greatly enhanced by the association of the surfactant tail groups forming hemimicelles (or admicelles). This is where the linear Region II begins. It has a greater slope than that of Region I. As surfactant concentration is increased even further, Region II gives way to Region III which describes nonlinear adsorption increasing less rapidly with concentration. Region III continues until the critical micelle concentration is reached. For solution phase concentrations greater than the CMC, adsorption is once again linear, but at a very small slope. This is because most surfactant added above the critical micelle concentration goes into the formation of micelles.

Louvisse and González (1988) developed isotherms for a nonionic surfactant (Triton X-100, an ethoxylated octyl phenol) on silica. When



(a)



(b)

Figure 2.3. Typical Anionic (a) and Nonionic (b) Surfactant Adsorption Isotherms (Lopata *et al.*, 1988; Louvisse and González, 1988)

the concentration of surfactant per unit surface area of sorbent was plotted against the log of the surfactant concentration an ogive (S-shaped curve) resulted, centered on the critical micelle concentration. The extent of adsorption increased from essentially zero to its maximum as surfactant concentrations increased over one order of magnitude. As with anionic surfactants, most of the nonionic surfactant added above the CMC formed micelles. Typical isotherms for anionic and nonionic surfactants are shown in Figure 2.3.

Schick (1987) reported increased adsorption for mixtures of anionic and nonionic surfactants. He attributed this to the formation of mixed adsorption layers on the adsorbent. Somasundaran *et al.* (1984) also reached similar conclusions. They found that nonionic polyether alcohols did not adsorb when in solution alone; however, when an alkyl sulfonate was present, the nonionic's adsorption was significant. The adsorption of the sulfonate also was enhanced.

Schwuger (1981), in contrast, reported different conclusions when studying the adsorption of an equimolar solution of SDS and octylphenol polyglycol ethers on carbon containing sorbents. He found that adsorption of the nonionic surfactant was not influenced by the presence of SDS which was hardly adsorbed at all. He reasoned that the nonionic surfactant is more strongly attracted to the carbon surface, while the SDS is largely displaced. Schwuger (1981) also found that adsorption of anionic surfactants increases with increased electrolyte content due to lower electrical repulsive forces.

The use of polymers such as polyacrylic acid and polyacrylamide as sacrificial adsorbates to decrease the adsorption of a mixed nonionic and anionic surfactant solution was investigated by Gebhardt and

Fuerstenau (1984). The sorbent used was hematite. They found that the presence of a pre-adsorbed anionic polymer significantly reduced the adsorption of an anionic surfactant but did not influence the adsorption of a nonionic surfactant. Schwuger (1981) reported similar results using sodium citrate and sodium triphosphate as the sequestrants, and aluminum oxides as the sorbent.

Lucassen-Reynders (1981) studied mixed anionic surfactant solutions with different valency counterions and found that there was a strong preference for the adsorption of the higher valency compounds. For anionic-cationic mixtures, he found that one-to-one mixtures behave like nonionic surfactants; they are surface active at much lower concentrations than the ionized constituents and are not affected by the presence of inorganic salts.

Huang (1980) described probable soil sorption mechanisms for various solution constituents. Of particular significance to this project are the mechanisms proposed for the adsorption of anionic and nonionic surfactants. Anionic surfactants adsorb primarily because of specific anion adsorption and electrostatic attraction, whereas nonionic surfactants (and many other nonpolar organic molecules) adsorb due to ion-dipole and coordination types of interactions as well as hydrogen bonding.

From these mechanisms, several possible interactions can be identified for a solution that contains surfactants and nonpolar hydrocarbons (contaminants) which also are adsorbed to soil. For example, anionic surfactant adsorption is considered "specific", and the strength of the sorptive interactions are much greater than the "nonspecific" interactions of the contaminants. In this case, if a sufficient number of

charged sites were available on a soil, the adsorption of an anionic surfactant could displace adsorbed contaminant hydrocarbon molecules from the soil matrix forcing them into solution. Nonionic surfactants, in contrast, adsorb via the same mechanisms as do nonpolar hydrocarbons. Since the energies of adsorption are similar in this case, the contaminants might not be displaced from the soil matrix at all. As mentioned previously, if the contaminant associates with a surfactant molecule that is subsequently adsorbed, apparent adsorption of the contaminant may actually increase.

Biodegradability of Surfactants

Swisher (1987) extensively investigated the biodegradation of surfactants. He related several reasonably well validated generalizations concerning the relationship between surfactant structure and biodegradation. These relationships are:

1. The structure of the hydrophobe group is very important in determining biodegradability. Biodegradability is promoted by increased hydrophobe linearity and deterred by hydrophobe branching.
2. The nature of the hydrophile has only a minor influence on biodegradability. Hydrophile influence is seen for polyethoxylate nonionics, where biodegradability is promoted by shorter ethoxylate chains.
3. For alkylbenzene sulfonates, increased distance between the sulfonate group and the far end of the hydrophobe group increases the speed of primary biodegradation (the longer the chain length, the faster the primary biodegradation).

Swisher's work also contains detailed biodegradation tables which include most of the surfactants currently produced.

Literature from surfactant manufacturers contains data on the biological degradation of each surfactant produced. For example, GAF Corporation tested their nonionic surfactants (the Igepal[®] line of

products) and report that these products have been shown to be readily subject to primary biodegradation. They have been demonstrated to biodegrade at efficiencies exceeding 90 percent within the EPA specified time period utilizing three different testing procedures; the Shake Flask Test, the River Die-away Test and the Semi-continuous Activated Sludge Test. These three tests were developed principally for anionic surfactants by the Soap and Detergent Association. They are generally recognized and used in assessing surfactant degradability (GAF, 1982). Numerous other tests (and several versions of those mentioned above) have also be used to determine surfactant biodegradation. Swisher (1987) reviewed these various test methods.

Toxicity of Surfactants

Swisher (1987) lists two major underlying factors pertinent for all types of surfactants concerning their toxic effects on microorganisms. These are: (1) the disruption of cellular membranes by interactions with their lipid structural components; and (2) the reaction of surfactants with enzymes and other proteins essential to the proper functioning of the cell. All surfactants, consequently, show antibacterial activity. The majority of the quaternary, cationic type are powerfully germicidal and many of them are toxic to humans. Anionic surfactants are relatively nontoxic, with LD₅₀s in the same range as sodium chloride and sodium bicarbonate. The nonionic surfactants generally are the least toxic towards humans and have the least activity against bacteria.

Each manufacturer provides toxicity information on the surfactants they produce. GAF Corporation (GAF, 1982) for example, reports the following information for the nonionic surfactant CO-630 (a nonylphenol with nine ethylene oxide groups):

1. acute oral toxicity for rats, $LD_{50} = 3 \text{ g/kg}$;
2. acute lethal concentration for Bluegill, $LC_{50} = 7.9 \text{ mg/L}$;
3. 100 humans tested for dermal irritation, not irritating; and
4. primary ocular irritation to rabbits, severe.

Clearly, the literature is replete with sufficient information to judge whether toxicity would preclude the use of any surfactants considered in this investigation.

Groundwater Transport of Organic Contaminants

Transport of organic chemicals by groundwater is commonly described using the advective/dispersive transport equation with a term to account for the sorption of the organic solute onto the soil matrix. For simplicity, this sorption term is often developed assuming local equilibrium and a linear relationship between the quantity of chemical in the adsorbed and dissolved phases. Assuming one-dimensional flow the mathematical form is given by (Freeze and Cherry, 1979)

$$\frac{\partial C}{\partial t} = D_t \frac{\partial^2 C}{\partial x^2} - v_t \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial S}{\partial t} \quad (2.17)$$

where

∂ = the partial differential operator,

$C(x,t)$ = aqueous solute concentration (kg solute/m³ water),

$S(x,t)$ = sorbed solute concentration (kg solute/kg soil),

D_t = Dispersivity (or dispersion coefficient) (m²/day),

n = aquifer porosity (m³/m³),

ρ_b = soil bulk density (kg soil/m³ bulk volume),

x = spatial coordinate (m),

t = time (day),

v_t = average flow velocity (m/day).

For linear and reversible sorption

$$K_d = S/C \quad \text{or} \quad K_d = \delta S / \delta C \quad (2.18)$$

and a mathematical manipulation yields

$$\frac{\delta C}{\delta t} + \frac{\sigma_b K_d}{n} \frac{\delta C}{\delta t} = D_t \frac{\delta^2 C}{\delta x^2} - v_t \frac{\delta C}{\delta x} \quad (2.19)$$

or

$$\frac{\delta C}{\delta t} \left[1 + \frac{\sigma_b K_d}{n} \right] = D_t \frac{\delta^2 C}{\delta x^2} - v_t \frac{\delta C}{\delta x} \quad (2.20)$$

The term in brackets is defined as the retardation factor, R .

$$R = 1 + \frac{\sigma_b K_d}{n} \quad (2.21)$$

Equation 2.21 shows that as the partition coefficient, K_d , increases, the retardation factor increases. This, in turn, leads to a decrease in the mobility of the contaminant because the retardation factor must always be greater than or equal to unity. Consequently, if the mobility of a contaminant can be increased, the partition coefficient is decreased leading to a decrease in the retardation factor. In a pump and treat remediation system, therefore, increased mobility is a desirable objective.

For example, Stauffer and MacIntyre (1986) determined that $K_d = 8.18 \pm 0.23$ for naphthalene on a soil. Substituting $K_d = 8.18$ into Equation 2.21, and assuming typical values of $\sigma_b = 1.8 \text{ kg/m}^3$ and $n = 0.30$, results in a calculated retardation factor of 50.1. The expected result of applying a surfactant solution is a reduction in the partition coefficient. If the partition coefficient could be reduced by one half ($K_d = 4.09$), the retardation factor would be decreased to 25.5. The effect would be to increase the mobility by 49 percent, which would

significantly decrease the volume of water and length of time required to remediate an aquifer using a pump and treat system to affect the remediation.

Valsaraj and Thibideaux (1989) derived an equation for estimating the retardation factor for surfactant micellar mediated transport of hydrophobic contaminants in groundwater.

$$R = 1 + \frac{K_{oc}[f_{oc}](1-n)\sigma_b/n}{1 + K_m v_w (C_{sur} - CMC)} \quad (2.22)$$

where

K_{oc} = partition coefficient for the contaminant between the soil (based on organic content of the soil, oc) and water (cm^3/g),

f_{oc} = fraction organic content of the soil (mass fraction),

n = porosity of the soil,

σ_b = bulk density of the soil (g/cm),

K_m = partition constant for hydrophobic compound between the micellar and aqueous phases (mole fraction ratio),

v_w = molar volume of water (L/mol),

C_{sur} = total concentration of surfactant (mol/L),

CMC = critical micelle concentration of the surfactant.

The authors developed a linear free energy relationship for estimating K_m from K_{ow} for eleven hydrophobic non-polar organic compounds partitioning into micelles formed from molecules of sodium dodecyl sulfate. They used this relationship plus a linear free energy relationship (Equation 2.13) relating K_{oc} and K_{ow} to simplify Equation 2.22 to yield

$$R = 1 + \frac{0.21(K_{ow})^{0.92}}{1 + 0.22(K_{ow})^{0.847}[C - CMC]} \quad (2.23)$$

The authors cautioned that this relationship does not take into account surfactant adsorption to soil. Also, the equations have not been evaluated to establish whether they adequately predict retardation in an actual or simulated aquifers. Both equations 2.22 and 2.23 predict a decrease in the retardation factor whenever the surfactant concentration is above the CMC.

CHAPTER III

OBJECTIVES

The review of the literature indicates that the state of knowledge regarding the use of surfactants for pump and treat aquifer remediation projects is inadequate. The use of such a process, where hazardous contaminants are rendered more mobile, could be very beneficial, but could also give rise to a greater environmental threat. Investigations involving enhanced oil recovery processes, surface soil decontamination efforts and commercial processes provide useful information, however, they do not directly address the concerns specific to surfactant use for a pump and treat system.

Technology transfer from enhanced oil recovery efforts are useful for addressing problems in the removal of organic compounds. However, this technology is designed to deal with distinct hydrocarbon and aqueous phases, and EOR objectives do not include the removal of the hydrocarbons to the low levels required in a groundwater system. As discussed in the literature review, the method of mobilization primarily is one of emulsification brought about by surfactant solutions designed to produce ultralow surface tensions and improve the wettability of the rock-fluid interfaces. Remediation of a contaminated aquifer, however, often involves aqueous phase systems with contaminant solution concentrations on the order of milligrams or micrograms per liter. Because solubilization rather than emulsification is the objective when formulating the surfactant solution, the desirable surfactant characteristics concerning such factors as CMC, interactions with the soil and

solubilization of the contaminant, may be much different than those required for the EOR process.

The U.S. EPA and others have performed research on the application of surfactant solutions to decontaminate surface soils. Primarily, their work consisted of a comparison of contaminant removal efficiencies with and without a surfactant present. Although this study demonstrated the efficacy of the process, it did not define the fundamental process parameters. Rigorous sorption studies were not performed to investigate many of the interactions that are likely to occur in a groundwater environment. Among those of concern are; (1) the kinetics of the sorption processes for both the surfactant and the contaminants, (2) how the interactions between the contaminant and the surfactant solution are affected by various soils having different mineralogical characteristics, and (3) how the contaminant partitioning process is quantitatively affected by using different surfactant concentrations. The last two items listed are due to the lack of detailed sorption isotherm studies. Also, an objective method has not been established for the surfactant selection process. All the surfactant characteristics of importance when used for groundwater remediation processes need to be identified, and a method of evaluation established to select the most appropriate surfactant or mixture of surfactants and the most efficient concentration for a particular application. Although surfactants have been used for groundwater remediation (MTARRI, undated), the only surfactant used was sulfonate (an anionic surfactant). Other surfactants need to be evaluated.

Accordingly, the goal of this research is to determine the effects of surfactants on the sorption of organic contaminants on aquifer

materials with an emphasis on the research needs identified above. To attain this goal, the following objectives were developed:

1. Determine suitable surfactant(s) for use to mobilize a contaminant in an aquifer.
 - A. Identify techniques to determine characteristics of surfactants.
 - (1) critical micelle concentrations.
 - (2) surfactant adsorption to soil.
 - (3) surfactant effect on contaminant release from soil.
 - (4) clay particle dispersion as a result of surfactant addition.
 - (5) toxicity and biodegradability of surfactant.
 - B. Provide general guidelines on surfactant selection based on the type of contaminant and soil characterization. The purpose is to provide the criteria for selecting a surfactant without having to rely on time-consuming and costly laboratory experimental studies.
2. Determine the effects of the selected surfactant(s) on sorption equilibria in a soil/contaminant/solution system.
 - A. Determine how various concentrations of surfactant(s) affect the partitioning of contaminant between the soil and the solution.
 - B. Determine the most efficient concentration of surfactant(s) for mobilizing the contaminant.
 - C. Determine the mechanisms by which surfactants mobilize the contaminant.
3. Determine the effects of the selected surfactant(s) on sorption in a dynamic system.
 - A. Determine how the surfactant solution affects contaminant release in a flow through column under various flow rates compared with a system using only water.
 - B. Determine whether the surfactant(s) influences the permeability of the soil matrix.
 - C. Determine how equilibrium partitioning (objective 2A) compares with partitioning in a dynamic system.

The model contaminant selected for this study was naphthalene. The aquifer material used as sorbents originated from South Carolina, Oklahoma and California. These materials will be fully described in the following chapter.

CHAPTER IV

MATERIALS AND METHODS

Experimental Plan

This investigation of the effect of surfactants on the desorption of organic contaminants from aquifer material was conducted in two phases. Phase I consisted of preliminary work involved with characterizing the contaminant, sorbents and surfactants as well as selecting the surfactant(s) to be used for the sorption studies. The characterizations are prerequisites for understanding the physical makeup of a soil/solution/contaminant system. Interpretation of the results from contaminant sorption studies is not possible without having a complete understanding of the system components. The selection of the most appropriate surfactant was made based on criteria established for the surfactant's interaction with the Charleston soil, with the intent that this surfactant then would be applied to other soil types to ascertain its performance with respect to its applicability for a pump and treat aquifer restoration program.

Phase II consisted of an examination of the equilibrium sorption effects and column response when using a surfactant solution to mobilize the selected contaminant, naphthalene. The equilibrium sorption effects of surfactant usage with each soil were quantified by developing sorption isotherms for different surfactant solution concentrations. Subsequently, column studies were conducted to investigate how the use of surfactant solutions could improve contaminant removal in a dynamic system.

Phase I

The materials required for this project included contaminants, soils and surfactants. After procuring these materials, the initial characterizations of each were conducted. Based on the results of these characterizations as well as additional experimental work, an appropriate surfactant solution was selected.

Characterizations

The individual characterization elements are diagrammed in Figure 4.1. The series of procedures performed to characterize the contaminants, surfactants, and soils are shown.

For the contaminants, sorption kinetic studies were performed on four soil types for trichloroethylene, dichlorobenzene and naphthalene. Factors considered were extents of adsorption, handling problems due to volatility and, for subsequent equilibrium sorption studies, the amount of solute-sorbent contact time required to ensure a that close approach to equilibrium was attained. In addition, biodegradation studies were performed to determine whether precautions were required to eliminate biodegradation as a factor for the sorption studies.

The critical micelle concentrations were determined in this phase of the project because it is a characteristic of the surfactant itself. The characteristics of surfactant interaction with aquifer materials were considered in the surfactant selection process described in the following section. The CMC was determined for the nine individual surfactants selected for screening as well as twelve 50:50 mixtures of the individual surfactants.

The soils were characterized to assess the influence of certain characteristics on sorption processes. Those considered were grain

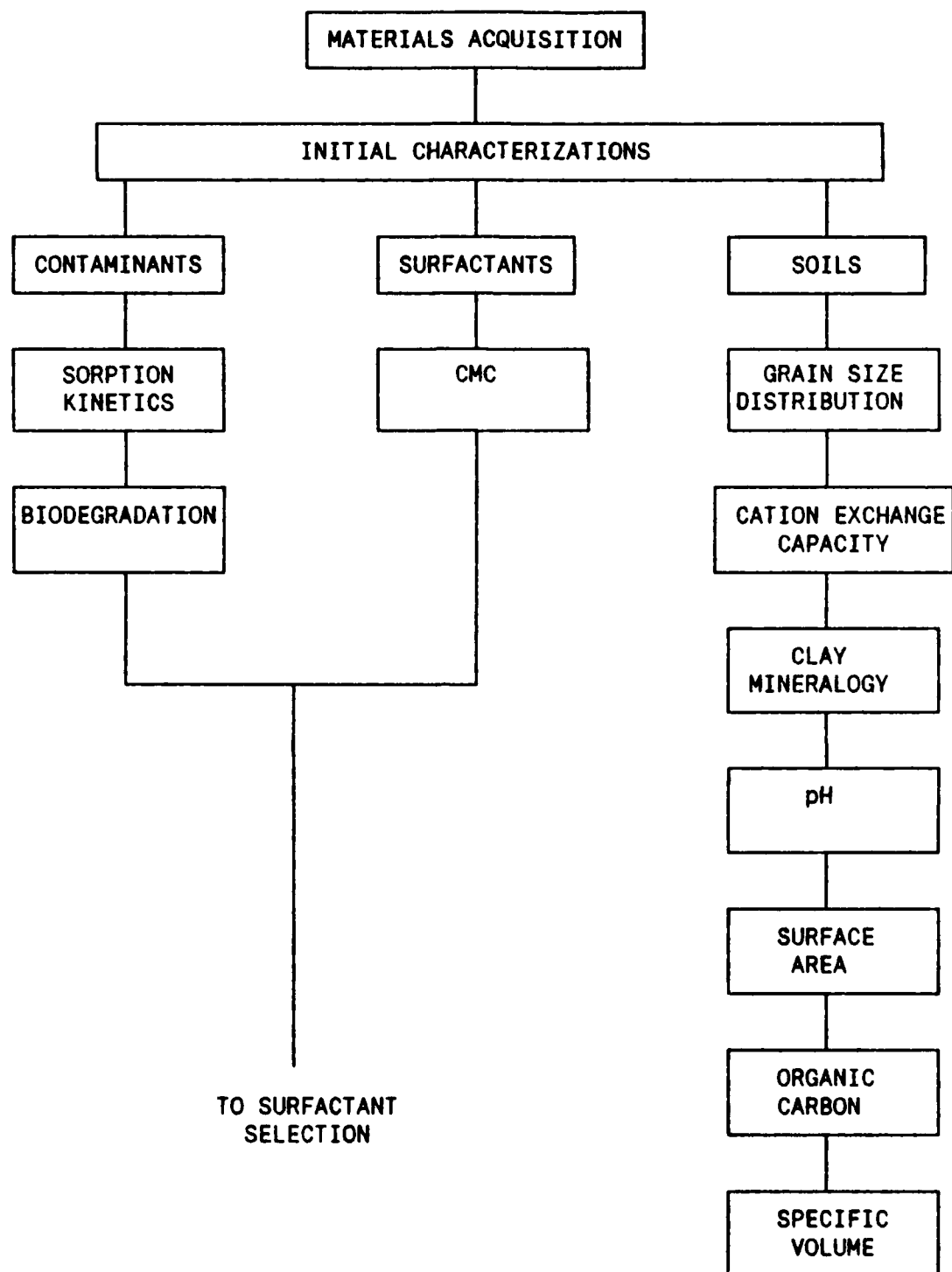


Figure 4.1. Experimental Plan: Phase I, Characterizations

size distribution, cation exchange capacity, clay mineralogy, pH, surface area, organic carbon content and specific volume.

Surfactant Selection

The objective of the surfactant selection process was to determine an appropriate surfactant solution for use in the sorption studies. It was decided that the surfactants were to be selected on the basis of their performance with the aquifer material showing the greatest sorptive reactivity, the Charleston soil. Once the surfactant was selected, it was to be used with the Charleston soil as well as the other three soil types to evaluate its performance in mobilizing the selected contaminant.

The soil-surfactant interactions investigated were the extent to which each surfactant adsorbs to the soil, how each surfactant affects the dispersion of clay particles and how each surfactant affects the solution concentration of the contaminant by contaminant solubilization from the soil. Also considered were adequate solubility of the surfactant, adequate biodegradability and minimal toxicity. Appropriate surfactants were those that exhibited relatively low adsorption to the soil, minimal clay dispersion, and good release of the contaminant from the soil. Solubility was observed during all laboratory procedures, and precipitates noted. Biodegradability and toxicity were considered after the most appropriate surfactants were selected. The components of the surfactant selection phase of the study are summarized Figure 4.2.

Phase II

The components of the various solute-sorbent-solution systems to be investigated in Phase II were identified and characterized in Phase I.

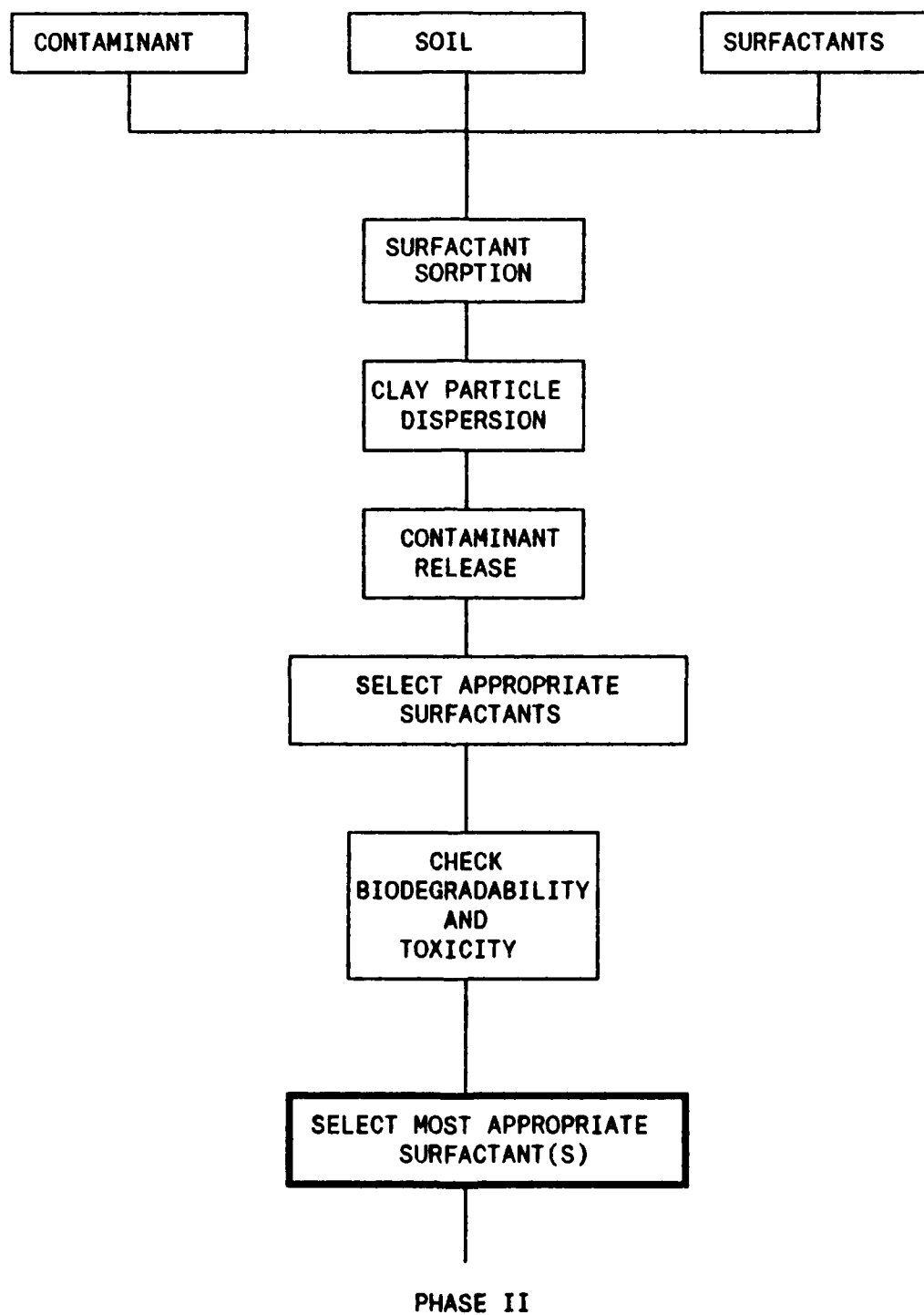


Figure 4.2 Experimental Plan: Surfactant Selection Process

Phase II consisted of two parts: equilibrium sorption studies and column studies.

Equilibrium Sorption Studies

The purpose of the equilibrium sorption studies was to determine the effect a surfactant solution has on the partitioning of a target contaminant between the soil and the solution phase. For each soil type, five adsorption isotherms were developed, all prepared in an identical manner. After equilibration and analysis, each set of samples was diluted with different concentrations of the surfactant solution. This allowed the development of sorption isotherms showing the partitioning of naphthalene between the soil and solution phases under the influence of varying amounts of surfactant.

The results of these tests identified the most effective surfactant solution concentration to be used in the column studies. Also, a comparison of the effectiveness of the surfactant solution to mobilize the contaminant among the various soil types could be made.

Column Studies

The column studies were performed to simulate the process of decontaminating a soil by the method currently used for pump and treat remediation efforts, water flushing, as well as using a surfactant solution at a concentration identified in the equilibrium sorption studies. The objectives of this phase of the project included comparing the efficiency in contaminant extraction between the water and surfactant floods, as well as investigating how different flow rates affect each process. The details of implementing this experimental plan are contained in the following paragraphs.

Materials Acquisition and Preparation

Contaminant

Contaminant Selection

The contaminant selected for this project is naphthalene. It was chosen because of its hydrophobic character typical of many groundwater contaminants. Also, it is a constituent of hydrocarbon fuels such as gasoline and jet fuels, and has been known to enter groundwater systems from fuel spills or leaking underground storage tanks.

The original intent of this project was to use a contaminant from the class of compounds that fall into the category of the low molecular weight, volatile chlorinated hydrocarbons, such as the common solvents including tetrachloroethylene (PCE) and trichloroethylene (TCE). Inquiries made to the various manufacturers of radio-labeled compounds showed that PCE was not available off the shelf, and would have to be synthesized at excessive expense. TCE was available, and 100 micro-curries of this radio-labeled compound were obtained. Preliminary experiments showed, however, that TCE adsorbed very little to the aquifer material. In addition, because TCE is extremely volatile it proved to be impossible to retain in sealed vials. A blank kinetic study using water with no soil showed a loss of 50 percent of the TCE during a two week period.

Because of negligible adsorption and the handling problems encountered due to volatility, TCE was not selected as the contaminant to be studied. A more hydrophobic and less volatile compound was sought. After a literature search and a check with suppliers, it was decided that 1,4-dichlorobenzene (DCB) would be appropriate, and 100 micro-curries were obtained. Although DCB adsorbed to a greater extent than did TCE,

volatility problems were still encountered. Once again, a kinetic study showed that the loss rate of DCB from a blank solution (approximately 45 percent in two weeks) was nearly as great as that of TCE. This loss rate was deemed unacceptable.

Thereupon, naphthalene, a nonpolar aromatic hydrocarbon composed of two benzene rings, was chosen because it is more hydrophobic than TCE and DCB, and has a relatively low Henry's constant indicating that volatility should be less of a problem. A blank kinetic study conducted with this contaminant showed that less than five percent of the naphthalene was lost after two weeks, and a preliminary experiment indicated that this compound would adsorb to the aquifer material. Since these studies indicated that naphthalene would be suitable, it was selected as the model contaminant for the duration of the investigation. Some of the physical and chemical characteristics of naphthalene are summarized in Table 4.1.

Preparation of Naphthalene Stock Solution

One hundred micro-curries of 14 carbon-labeled naphthalene with a specific activity of 4.7 mCi/mmol and a purity of greater than 98 percent were purchased from Sigma Chemical Company. The naphthalene arrived as a crystalline solid in a screw cap vial. The following procedure was used to prepare the naphthalene stock solution:

1. Distilled water was prepared by bubbling nitrogen gas through approximately 1.0 L for one hour to purge oxygen gas. This was done to preclude oxidation of the naphthalene as well as limit any possible biodegradation.
2. A 240 mL amber bottle was soaked overnight in a solution consisting of concentrated sulfuric acid saturated with sodium dichromate. The bottle then was rinsed several times with distilled-deionized water and allowed to dry.

Table 4.1. Physical and Chemical Characteristics of Naphthalene

Characteristic	Value	Source
Molecular weight	128.17 g/mol	(Weast, 1986)
Boiling point	218°C	(Weast, 1986)
Melting point	80.5°C	(EPA, 1979)
Vapor pressure at 20°C	0.0492 torr	(EPA, 1979)
Solubility in water at 20°C	34.4 mg/l	(EPA, 1979)
Log octanol-water coefficient	3.37	(EPA, 1979)
Henry's Law constant (25°C)	0.02	(Lion, 1983)
Density	0.9625 g/ml	(Weast, 1986)
Dipole moment	0 (in benzene)	(McClellan, 1963)
Electronic Polarizability	16.5(10 ⁻²⁴)cm ³	(Weast, 1986)

3. The bottle, a Mininert^R valve and a magnetic stirrer were weighed, and this weight was used as a blank weight to estimate the amount of water later added to the bottle. The weight was 185.4 g.
4. The bottle with the magnetic stirrer inside was filled approximately half full with the prepared water. The screw cap vial containing the naphthalene was opened, the cap discarded, and the vial submerged in the bottle. The bottle then was filled to near capacity with prepared water, and capped with the Mininert^R valve. The solution so prepared is termed the "naphthalene stock solution."
5. The bottle containing the naphthalene stock solution was placed on a magnetic stirrer overnight to ensure solubilization of all the naphthalene.
6. The bottle and its contents then were weighed to estimate the volume of solution. This weight was 423.3 g. Since the weight of the vial was 11.5 g, the mass of water was calculated at 226.4 g. Using 1.0 g for each mL of water, the volume of naphthalene stock solution was estimated to be 226.4 mL.
7. Three 0.10 mL samples were removed from the bottle using a micro-syringe inserted through the Mininert^R valve, injected into 10 mL of liquid scintillation cocktail, and counted using the liquid scintillation counter. The counts were 79107.50 dpm, 81070.05 dpm, and 81784.56 dpm; with an average equal to 80654.04 dpm.
8. Since 1 μ Currie = 2.2×10^6 dpm, the total radioactive activity of the naphthalene stock solution was calculated to be

$$\text{Activity} = \frac{80654.04 \text{ dpm}}{0.10 \text{ mL}} \times 226.4 \text{ mL} \times \frac{1 \text{ } \mu\text{Ci}}{2.2 \times 10^6 \text{ dpm}} \quad (4.1)$$

$$\text{or Activity} = 83.000 \text{ } \mu\text{Ci}.$$

9. The naphthalene stock solution was placed in a 3°C refrigerator and stored for subsequent use.

Sorbents

Sources

The objective in searching for aquifer sorbent materials was to use various aquifer materials with different physical characteristics such as organic carbon and clay content. Contacts were made with individuals at the following locations: Tinker Air Force Base, Oklahoma City, OK;

Sacramento, CA; Albany, GA; and Charleston and Greenville, SC. A listing of the soil materials received as a result of these contacts is given in Table 4.2. The samples from California and Georgia were received in numerous containers (approximately 200-500 ml) representing soil from small ranges in depth. The other samples were received in 5 gallon buckets.

Preparation of Sorbents

The sorbents used for this project were the Greenville soil, Tinker soil, Charleston soil and California soil. The Georgia soil was not used for three reasons: (1) there was a very limited supply of the soil; (2) the depths from which the soil samples were taken were extremely great (290-510 ft) with little possibility of contamination at these depths; and (3) the samples were almost totally silica sand, with no organic material or clay. Because of this, sorption effects would be negligible.

The Greenville, Tinker and Charleston soils arrived in a water-saturated condition. These soils were placed on large aluminum sheets and allowed to air-dry. The California soil was received in a dry condition. All of the soils were ground with a mortar and pestle and sieved through a 2.0 mm sieve to remove gravel and other debris. The fraction passing the sieve, less than 2.0 mm, was used for characterizing the soil, and was planned for use in the column studies. A portion of the soil passing the 2.0 mm sieve was sieved again to retain only those particles smaller than 250 μm . This fraction, which represents the clay, silt, very fine sand and fine sand fractions (Brady, 1984) was used for all batch studies. The rationale for using only those particles smaller than 250 μm in the batch studies is two-fold. First of

Table 4.2. Aquifer Material and Sources

Source	Amount	Depth of samples	Water Table
Tinker AFB, Oklahoma City, OK; U.S. Army Corps of Engineers	5 gals	80-100 ft	70-75 ft
McClellan AFB, Sacramento, CA; U.S. Air Force	3 gals	175-500 ft	70-80 ft
Warner Robins AFB, Atlanta, GA; Layne-Atlantic Company, Albany, Ga	1 gals	290-510 ft	14-15 ft
Charleston AFB, Charleston, SC; U.S. Air Force	10 gals	8-10 ft	7-8 ft
Industrial site, Greenville, SC; RMT, Inc. Greenville, SC	5 gals	9-14 ft	8-9 ft

all, using only the smaller particles provided for a more uniform and homogeneous suspension in the batch reactor vials. Also, because of the high relative surface area associated with the smaller particles, the vast majority of sorption that occurs is due to these particles. After processing, all soils were stored at room temperature in 2.0 liter Nalgene[®] plastic containers.

Surfactants

Sources

Seventeen companies that produce surfactants were contacted by written communication explaining the objectives of the proposed project and requesting information concerning their products. Five replies were received. Based on a review of the literature and discussions held with representatives of the various companies, samples of surfactants listed in Table 4.3 were obtained.

The asterisks in Table 4.3 identify those surfactants chosen for screening for use in this investigation. These choices were made based on a review of the manufacturers' literature obtained along with each sample. Considerations included toxicity, solubility, duplications and possibilities of mixtures. A listing of the mixtures of surfactants that were screened in addition to the nine primary surfactants indicated in Table 4.3 is given in Table 4.4. The selection of these particular mixtures was made for various reasons. The literature search showed that mixtures can improve soil sorption characteristics, have beneficial effects on critical micelle concentrations, and greatly decrease interfacial tensions. Some of these mixtures were selected based upon recommendations made by manufacturers. Also, because three different classes of mixtures could be formed (i.e., nonionic-nonionic, nonionic-anionic,

Table 4.3. Surfactant Samples Obtained from Manufacturers

Company	Surfactant	Type
ICI Americas	Tween 80	Nonionic
	Myrj 52S	Nonionic
	Brij 98	Nonionic
	Ahcowet RS	Anionic
	Atlox 3409F	Anionic-Nonionic Blend
Grace Chemical Co.	Hamposyl L	Anionic
	Hamposyl L-30*	Anionic
	Hamposyl C	Anionic
	Hamposyl C-30*	Anionic
Cyanamid	Aerosol TR-70	Anionic
	Aerosol AY-65*	Anionic
Atkemix	Brij 700	Nonionic
	G-2200*	Anionic Blend
	Tween 20*	Nonionic
	Tween 60*	Nonionic
GAF Chemicals	Igepal CO-630*	Nonionic
	Igepal CO-730	Nonionic
	BP-769*	Anionic
	RP-710*	Anionic

Table 4.4. Surfactant Mixtures

Type of Blend	Surfactants
Nonionic - Nonionic	Tween 20 - Tween 60
	Tween 20 - Igepal CO-630
	Tween 60 - Igepal CO-630
Nonionic - Anionic	Tween 20 - Hamposyl L-30
	Tween 20 - Aerosol AY-65
	Tween 60 - RP-710
	Igepal CO-630 - RP-710
	Igepal CO-630 - Hamposyl C-30
Anionic - Anionic	Igepal CO-630 - Aerosol AY-65
	BP-769 - R-710
	Hamposyl L-30 - Aerosol AY-65
	RP-710 - Hamposyl C-30

anionic-anionic), selections from the nine primary surfactants were made to ensure that each class would be represented.

Preparation of Surfactant Stock Solutions

Each surfactant sample arrived in approximately eight ounce bottles. Three of the surfactants arrived in a diluted state (Hamposyl C-30, 30 percent; Hamposyl L-30, 30 percent; and Aerosol AY-65, 65 percent). A ten percent surfactant solution on a volume basis was prepared for each of the nine primary surfactants by pipetting an appropriate volume of each into a 1.0 L volumetric flask which was subsequently filled with distilled water. These solutions then were transferred into 1.0 L amber bottles and capped with teflon lined screw caps.

The twelve surfactant mixtures were prepared by pipetting 100 mL of each constituent surfactant solution into a 240 mL amber bottle. This resulted in 200 mL of a 10 percent surfactant solution (each surfactant contributing 5 percent). These bottles also were capped with a screw cap and teflon lined septa. It was decided that a 50:50 mixture of surfactants be used for two reasons. First, the surfactant mixtures used previously for soil decontamination studies reported in the literature were all prepared on this basis. Secondly, preparing more than one volumetric ratio of constituent surfactants would have resulted in an excessive number of surfactant solutions that needed to be screened during the preliminary investigations. All of the surfactant stock solutions were stored at room temperature.

Equipment

The following pieces of equipment were used in the experimental phase of this project:

1. Beckman Liquid Scintillation Counter (LSC), Model LS 3801;
2. Beckman Acta CIII UV-visible Spectrophotometer;
3. Perkin-Elmer LS-5B Luminescence Spectrometer;
4. BET Quantisorb Sorption System;
5. Fisher Autotensiomat Surface Tension Analyzer;
6. Perkin-Elmer Atomic Adsorption Spectrophotometer, Model 306;
7. Phillips Electronics X-Ray Diffraction Unit, Type 15010000;
8. Sorvall SS-3 Automatic Superspeed Centrifuge;
9. Hach Ratio Turbidimeter, Model 18900;
10. Orion pH meter, Model 611;
11. Beckman RB3 Solu Bridge Conductance Meter;
12. Beckman RA4 Solu Meter Conductance Meter;
13. Haake-Buchler MCP2500 Microprocessor Pump.

Preliminary Experiments

The preliminary experiments were designed to characterize the components of the sorbent-solvent-solute system, as well as identify the conditions under which the components would be brought together for study. These experiments included soil characterizations, surfactant characterization, and naphthalene sorption kinetic studies. Before discussing the procedures used for these individual preliminary studies, explanations are presented regarding general procedures used throughout this project. These include two facets of samples preparation, the manner in which ionic strength and pH were poised for all phases of this study, and how mass adsorbed and solution concentrations were calculated using disintegration per minute (DPM) information obtained by liquid scintillation counting.

General Procedures

Glassware

Samples for several of the experiments conducted as part of this investigation were prepared in a similar manner. Whenever glassware came in contact with naphthalene or surfactants, the glassware was prepared in the following manner:

1. The glassware was washed with a detergent solution and rinsed with tap water.
2. A bath consisting of concentrated sulfuric acid saturated with sodium dichromate was prepared. All glassware was placed in this bath and allowed to soak for several hours.
3. The glassware then was removed from the acid bath, rinsed a minimum of five times with distilled water and air dried. This glassware was stored inverted until used.

This procedure is henceforth termed "acid wash".

Soil Sterilization

Another procedure used frequently was soil sterilization. A kinetic study of naphthalene adsorption to Greenville soil showed a substantial increase in rate of naphthalene loss from solution beginning after approximately three days of contact. The response appeared similar to a biodegradation response with an initial lag period. On this account, one to two drops of liquid from ten samples of each soil type and blanks were placed in test tubes with nutrient broth and incubated for three days. All of the samples showed positive growth. Agar plates then were prepared using naphthalene as the sole carbon source, streaked with sample supernatant, and incubated. Examination after incubation revealed that eight of the 40 plates showed positive growth, with at least one positive plate for each soil type. Consequently, the decision to sterilize all soils as part of the sample preparation procedure was made.

The soils were sterilized in a manner similar to that described by Skipper and Westerman (1972) using propylene oxide. Other methods considered were heating, autoclaving and adding sodium azide to poison the aqueous solution. The use of propylene oxide was selected because it is least likely to affect the soil's surface characteristics.

To sterilize each sample, approximately 0.1 mL propylene oxide was added to the sample vial (experimental unit) per gram of soil in the sample. After addition, the vial was plugged with a foam stopper and capped with a screw cap with a teflon lined septa. These samples then were wrapped in Saran Wrap and incubated at 30°C for 48 hours. This allowed the propylene oxide to volatilize and subsequently sterilize the soil. Thereafter, the samples were removed from the incubator, unwrapped and placed in a vent hood, whereupon, the caps were removed, and the propylene oxide allowed to vent through the foam plug for a minimum of two days. The foam plug was not removed until final assembly of the experimental unit in a contamination control hood. To minimize subsequent recontamination, all dilution water and burettes used for making the samples were autoclaved. This procedure is termed "soil sterilization."

Ionic Strength and pH

Because sorption is affected by changes in ionic strength and pH, a literature search and several experiments were conducted in order to decide whether experimental control over these two system variables was required. Investigations into the control of pH and ionic strength began with a review of procedures used in published papers concerning sorption of organic contaminants on soils. Sixteen published reports were reviewed (Banerjee *et al.*, 1985; Caron *et al.*, 1985; Curtis *et al.*,

1986; Fu and Luthy, 1986; Huang and Liao, 1970; Karickhoff et al., 1979; Katz and Uchrin, 1986; Lion and Garbarini, 1983; Miller and Weber, 1986; Rogers and McFarlane, 1980; Rogers and McFarlane, 1981; Schwarzenbach and Westall, 1981; Stauffer and MacIntyre, 1986; Talbert and Fletchall, 1965; Voice et al., 1983; Wahid and Sethunathan, 1979). Although only two of the researchers reported buffering pH for their experimental work, control of ionic strength (or concentration of calcium ions) was more prevalent. The most common additive was CaCl_2 to produce a 0.01M solution. Experiments then were planned to provide insight regarding the sensitivity of pH and ionic strength for the solutions planned for use in this project.

The objective of these experiments was to investigate variations in pH and ionic strength anticipated during the experimental phase of this investigation. Three experiments were performed. The first involved determining solution pH as a result of surfactant addition. The second focused on determining the pH and ionic strength of solutions containing the four soil types at various soil to solution ratios. The last experiment was performed to determine how the pH and ionic strength affected sorption of a surfactant to the Charleston soil. After presenting the results of these experiments, the rationale for establishing the experimental conditions with respect to pH and ionic strength is presented. This includes interpreting the results of the experiments as well as considering information obtained from the literature.

Variations in pH due to Surfactant Addition

Since different concentrations of surfactants were to be used for the naphthalene desorption studies, surfactant dilutions were prepared

to determine their effect on pH. The experiments were conducted using only the nine primary surfactants. It was assumed that pH variations for the mixtures would be similar, since the mixtures were prepared from the primary surfactants. Solutions were prepared by diluting appropriate volumes of surfactant stock solution with distilled water to produce surfactant concentrations ranging from 0.1 to 10.0 percent. The pH of each dilution was measured, and the results are shown in Table 4.5. Four of the samples were not analyzed due to experimental problems. Nonetheless, because sufficient information was available to establish pH ranges without these readings, it was not deemed necessary to repeat these studies.

The range of surfactant concentrations planned for use in the naphthalene desorption study was approximately two orders of magnitude, although, at this stage of the project, the exact concentrations were not known. For this concentration range, the results presented in Table 4.5 indicate that the pH probably would not vary more than approximately 1 pH unit within each surfactant type. Among the different surfactants, pH varied up to more than 6 pH units for the same concentration. Addition of surfactants S-1 and S-9, both anionic phosphate ester acids, resulted in very low solution pH. All nonionic surfactants, as well as the anionic surfactants S-3 and S-4, had only small effects on solution pH in the range of 4 to 5. Two surfactants, S-5 and S-6, actually increased solution pH. Grace Chemical Company (1986), reported that the pH for a 10 percent aqueous solution of S-5, a sodium lauryl sarcosinate salt, was in the range of 7.5-8.5. The significance of these results to subsequent experimental work planned for the project is discussed following a presentation of two additional experiments.

Table 4.5. Solution pH for Surfactant Dilutions in Distilled Water

Surfactant	0.1%	0.2%	0.3%	0.5%	1.0%	3.0%	10.0%
RP-710 (S-2) Anionic	2.82	2.52	2.36	2.47	----	1.54	----
Tween 60 (S-2) Nonionic	4.20	4.08	----	4.14	----	3.74	4.19
Aerosol AY-65 (S-3) Anionic	4.30	4.58	4.78	4.94	4.97	4.01	4.03
Hamposyl C-30 (S-4) Anionic	3.92	4.41	4.14	4.84	4.65	4.04	4.13
Hamposyl L-30 (S-5) Anionic	6.68	6.73	6.83	6.62	7.51	7.64	7.94
Atlas G-2200 (S-6) Anionic	6.78	7.28	7.36	7.40	7.37	7.36	7.47
Igepal CO-630 (S-7) Nonionic	5.55	5.38	5.26	5.12	5.02	5.59	6.15
Tween 20 (S-8) Nonionic	4.94	4.95	4.62	4.69	4.59	4.81	4.79
BP-769 (S-9) Anionic	2.82	2.54	2.42	2.37	2.14	1.82	1.52

Ionic Strength and pH at Different Soil:Solution Ratios

The objective of this experiment was to determine how ionic strength and pH varied within each soil type as a result of different soil:solution ratios, and how these characteristics varied among the soil types. The experimental units for each soil were prepared by introducing five different soil masses ranging from 5.0 to 25.0 grams of soil into 30 mL Nalgene plastic bottles containing 25.0 mL of distilled water. The samples were mixed on a rotating tumbler overnight, and the soil subsequently allowed to settle for one hour. The pH and specific conductance of the supernatant solution then were measured for each sample.

The results of this experiment are shown in Table 4.6. The ionic strengths (I) were estimated using an approximation provided by Snoeyink and Jenkins (1980) for surface waters:

$$I = (1.6 \times 10^{-5}) \times (\text{Specific Conductance}). \quad (4.2)$$

Although this is an estimate for surface waters, the relative values were of interest, and this approximation was sufficient for making the comparisons. It is clear that the pH within each soil type is influenced only minimally by the soil:solution ratios in the range considered. The pH differences among soil types, however, are much more pronounced. As far as ionic strength was concerned, there were only minor variations within each soil type at various soil:solution ratios or among the soil types. All values of ionic strength were relatively low. Once again, the significance of these results will be discussed following a presentation of one additional experiment.

Table 4.6. Ionic Strength and pH of Various Soil-solution Ratios

Mass soil (gms)	pH	Specific conductance ($\mu\text{mho/cm}$)	Ionic strength
Charleston			
5.0	5.57	50.0	0.00080
10.0	5.79	48.5	0.00078
15.0	5.72	50.0	0.00080
20.0	5.48	100.0	0.00160
25.0	5.64	50.0	0.00080
Tinker			
5.0	9.20	66.0	0.00106
10.0	9.32	74.0	0.00118
15.0	9.12	98.0	0.00157
20.0	9.15	125.5	0.00201
25.0	9.30	107.5	0.00172
Greenville			
5.0	5.85	42.0	0.00067
10.0	5.90	26.0	0.00042
15.0	5.87	40.0	0.00064
20.0	5.78	35.0	0.00056
25.0	5.89	22.5	0.00036
California			
5.0	7.35	75.0	0.00120
10.0	7.92	105.0	0.00168
15.0	7.95	131.0	0.00210
20.0	7.84	160.0	0.00260
25.0	7.83	207.5	0.00332

Ionic Strength and pH effects on Surfactant Sorption

Because surfactant interaction with soils was anticipated to have a significant influence on the results obtained from the equilibrium sorption studies, these experiments were designed to determine how varying ionic strength and pH affected surfactant sorption. Once again, the nine primary surfactants were used, and the Charleston soil was selected for use as the sorbent. Observations obtained from these experiments are presented in Table 4.7. For the uncontrolled experiments, the pH listed resulted from mixing five grams of Charleston soil with 25 mL of a 0.5 percent surfactant solution prepared from distilled water. The samples were mixed by placing them in a rotating tumbler overnight and then allowed to settle for one hour before the pH was measured. Subsequently, approximately 5.0 mL of the supernatant were placed into a 5.0 mL microvial and centrifuged at 6000 rpm for thirty minutes. The supernatant from the microvial subsequently was assayed for surfactant concentration using ultraviolet spectroscopy.

For experiments in which the pH was adjusted, the samples were prepared identically to the uncontrolled samples, except that the pH was adjusted prior to placing them on the rotating tumblers. This was accomplished by shaking the samples by hand and subsequently allowing the soil to settle for approximately one hour. Then either 0.01N HCl or NaOH was added to each vial to adjust the pH to approximate the pH of the Charleston soil (pH = 5.64). The samples prepared with 0.01M CaCl₂ were treated similarly except that all dilutions were prepared with 0.01M CaCl₂ instead of distilled water. The pH was not controlled in these samples.

Table 4.7. Results of Adjusting pH and Ionic Strength on Surfactant Sorption to Charleston Soil

SURF.	UNCONTROLLED		pH ADJUSTED			0.01M CaCl ₂	
	pH	percent adsorbed	pH before contact	pH after contact	percent adsorbed	pH	percent adsorbed
S-1	3.60	54.7	5.68	4.01	68.0	2.71	56.0
S-2	5.29	94.1	5.58	5.08	84.9	4.76	80.3
S-3	5.12	45.8	5.59	5.00	48.5	4.75	16.7
S-4	5.09	39.1	5.39	5.04	33.9	4.78	12.3
S-5	6.80	11.7*	5.45	6.04	62.9	5.87	73.9**
S-6	6.50	75.8	5.59	6.26	23.4	6.61	47.5**
S-7	5.55	95.7	5.52	5.90	96.4	4.94	98.2
S-8	5.53	76.8	5.58	5.40	73.1	4.83	77.6
S-9	3.38	57.0	5.38	3.70	63.2	2.35	60.9

* A Slight tinge was noted in the supernatant indicating insufficient solids separation. This probably caused an erroneous high solution concentration resulting in the false indication of little surfactant adsorption.

** A large amount of white precipitate formed when the surfactant was added. These values reported are most likely not indicative of the actual extent of adsorption.

An examination of the data recorded in Table 4.7 led to several observations. The adsorption of the nonionic surfactants (S-2, S-7 and S-8) was affected only slightly by the adjustments in pH and ionic strength. All other surfactants were anionic surfactants. With the exception of S-6, solution pH influenced the adsorption of the surfactants only minimally. For surfactant S-6, however, the results showed that for a relatively small pH change, 6.50 to 5.59, the fraction sorbed was reduced from 75.8 to 23.4 percent. This result does not appear likely and may be due to an analytical error. Also, it was noted that for the experiments where pH was controlled, the pH after contact was not the same as when the samples were prepared initially. It appeared that the pH shifted toward the pH of the uncontrolled sample. This most likely occurred because the pH of the supernatant solution was adjusted with acid or base prior to mixing the samples on the rotating tumbler. The shift in pH was caused by hydrogen ions sorbing onto or off of the soil surfaces which was only apparent after sufficient soil/solution contact time.

Poising the ionic strength with 0.01M CaCl_2 either showed decreased or an insignificant effect on sorption for the anionic surfactants. The decrease in surfactant sorption is not uncommon, as Bernard (1975) related that surfactant sorption decreases as salinity increases for EOR processes. This occurs because increased electrolyte content decreases the CMC due to a lowered electrostatic repulsion between the ionic head-groups (Slöjblom and Söderlund, 1985). In some cases, more of the anionic surfactant is associated with micelles and does not adsorb to soil surfaces.

Based on the results of these experiments as well as experiments reported in the literature, the experimental conditions with respect to pH

and ionic strength were established. For pH, the variations within each soil type would not be greater than approximately 1 pH unit for each particular surfactant. Although no pH variation is the ideal, it was decided that a variation of 1 pH unit was not excessive and would be acceptable for this study. Among soil types, however, there were greater differences in pH. The effects that these differences may have on sorption processes could be significant, particularly for the Tinker soil as compared with the Charleston and Greenville soils with their relatively low pH. However, having pH differences among the soils was one of the objectives for acquiring different soil types at the outset of this project, since this represents field conditions likely to be encountered. The pH was also shown to vary for the Charleston soil depending on which surfactant was added. Although the experiment was not conducted with different soils, it is likely the results would have been similar. This, however, was only a concern during the surfactant selection process, because once the surfactant to be used for the naphthalene desorption studies was selected, no other surfactants would be used. Based on this information, it was decided that pH would be allowed to vary for all phases of the project. However, to preclude pH variations due to hydrogen ion sorption on soil surfaces as previously discussed, all solutions would be adjusted to approximate the soil pH prior to contact with the particular soil.

In the case of ionic strength, however, surfactant addition, particularly ionizing surfactants, at various concentrations would have a pronounced effect on the ionic strength of the resulting solutions because all ionic strengths were fairly low. The variations anticipated within and among the soil types were of a magnitude which could confound

sorption results. Consequently, a 0.01M CaCl_2 solution was used to prepare all surfactant and soil solutions for all sorption studies. This "swamping electrolyte" removed ionic strength as a variable for studies conducted within and among soil types. An added benefit was that soil-solution separation during centrifugation was facilitated in batch experiments by the presence of the electrolyte.

Some of the preliminary surfactant screening characterizations were conducted using water that did not contain the swamping electrolyte. All CMC's were determined using distilled-deionized water in accordance with the analytical procedure. Also, the single point surfactant sorption screening studies were conducted using distilled water. The clay particle dispersion determinations were conducted with distilled water because the electrolyte solution destabilized nearly all the colloidal material, regardless of the surfactant used, causing it to settle.

Since these studies, particularly the CMC determination and the single point sorption study, were not conducted under the pH and ionic strength conditions planned for the naphthalene equilibrium sorption studies, additional experiments were planned for the surfactant selected for use in these studies. These experiments, detailed later in this report, involved determining the CMC of the selected surfactant using the swamping electrolyte and adjusting the solution pH to approximate the soil solution pH for the soils used. Also, an adsorption kinetic study was conducted and an adsorption isotherm was developed for the selected surfactant with the Charleston soil using the swamping electrolyte solution to prepare the samples.

To summarize the experimental conditions specified as a result of these investigations:

1. For preliminary surfactant screening experiments (pH buffering was not used).
 - A. CMC determinations were made using distilled-deionized water for solution preparation.
 - B. Surfactant sorption experiments were conducted using distilled water for solution preparation.
 - C. Clay particle dispersion determinations were made using distilled water.
 - D. Contaminant release experiments were conducted using 0.01M CaCl_2 solutions. All surfactant solutions were adjusted to the soil pH prior to contacting them with the soil using either NaOH or HCL.
2. The surfactants selected for use in this study were then subjected to further evaluation to ascertain their sensitivity to pH and ionic strength effects regarding CMCs and surfactant sorption.
 - A. Two additional CMC determinations were made using a 0.01M CaCl_2 solution at pH's of approximately 5.5 and 7.0.
 - B. Surfactant sorption; Using the Charleston soil, a surfactant adsorption kinetic study was conducted and an isotherm was developed for a solution ionic strength of 0.01M CaCl_2 .
3. For batch and column contaminant sorption studies 0.01M CaCl_2 water was used for all dilutions. The solutions were not pH buffered.

Calculations Using the Liquid Scintillation Counter DPM Data

The contaminant release studies, kinetic sorption studies and sorption isotherm studies were conducted using ^{14}C carbon-labeled naphthalene. Analyses were performed utilizing a liquid scintillation counter (LSC) to determine the solution phase disintegrations per minute (DPM). An explanation as to the use of the LSC for analysis is presented followed by the mathematical calculations used to determine solution concentrations and masses adsorbed from DPM data.

Liquid Scintillation Counter

The LSC was programmed in accordance with the operating manual to count each scintillation vial once for 10 minutes or to obtain a confidence level of 95 percent of ± 1.0 percent, whichever occurred first. This means that in 95 out of 100 times, the counts are within ± 1.0 percent of the mean. The system used a set of standardized background quench curves programmed into the instrument to convert counts per minute to disintegrations per minute.

A sample was prepared for counting by taking a reaction vial to be analyzed and centrifuging it for thirty minutes at 6000 rpm. One mL was microsyringed from the supernatant of the sample and injected into 7.0 mL of liquid scintillation cocktail in a 20 mL scintillation vial. The cocktail consists of xylene, surfactant and fluor molecules (molecules that fluoresce). A volume of 7.0 mL was experimentally determined to be the minimum volume required to completely solubilize one mL of aqueous solution. The use of a minimal volume of cocktail was desired to avoid generating excessive waste material for subsequent disposal. After injecting the aqueous solution into the cocktail, the scintillation vial was sealed and placed in a rack for automatic counting on the LSC. The instrument's output presented disintegrations per minute along with a confidence level which, in most cases, was 1.0 percent.

Calculations of Masses and Concentrations

The input data required to calculate the mass of naphthalene adsorbed per gram of soil and the solution concentration of naphthalene for each reaction vial are:

1. mass of soil in the sample, and the specific volume of the soil (M_s , g; S_v , mL/g);

2. volume of water added to the vial (V_w , mL);
3. volume of naphthalene stock solution added to the vial (V_n , mL);
4. for the adsorption studies, the total mass of naphthalene in the vial (M_{nt} , μg) was obtained by injecting the same volume of naphthalene stock solution into blanks containing no soil. These blanks were analyzed using the LSC after the appropriate soil/solution contact time. The resulting DPM/mL then was manipulated to calculate the total mass of naphthalene in the vial.

$$M_{nt} = \frac{\text{DPM/mL} \times 128.2 \mu\text{g}/\mu\text{mol}}{(2.2 \times 10^6) \text{ DPM}/\mu\text{Ci} \times 4.7 \mu\text{Ci}/\mu\text{mol}} \times (V_w + V_n) \quad (4.3)$$

where

DPM/mL = LSC output for counting one mL of solution,

128.2 $\mu\text{g}/\mu\text{mol}$ = molecular weight of naphthalene,

$(2.2 \times 10^6) \text{ DPM}/\mu\text{Ci}$ = conversion factor to convert DPM to microcurries,

4.7 $\mu\text{Ci}/\mu\text{mol}$ = specific activity of the ^{14}C carbon labeled naphthalene;

5. the DPM determined by LSC (DPM).

The input data was entered into a computerized spreadsheet program.

The spreadsheet was formatted to make the calculations for determining naphthalene adsorption data for kinetic responses as well as equilibrium sorption isotherms. The calculations were made by a mass balance according to the following procedure:

1. The volume of the soil (V_s , mL) was determined by multiplying the mass of soil by its specific volume.

$$V_s = M_s \times S_v \quad (4.4)$$

2. The total volume of additives (V_t , mL) to the vial was estimated by adding the volumes of soil, water and naphthalene stock solution.

$$V_t = V_s + V_w + V_n \quad (4.5)$$

The value of V_t is only an estimate because the soil adsorbs water, and the resulting swelling is not necessarily proportional to the amount of water adsorbed.

3. The total volume of a reaction vial was experimentally determined to be 6.18 mL. The volume of air (V_a , mL) was then calculated.

$$V_a = 6.18 - V_t \quad (4.6)$$

The volume of air was later used to estimate the amount of naphthalene in the gas phase within the vial.

4. The concentration of naphthalene in solution (C , mg/L) was calculated by converting DPM/mL obtained from the LSC output to concentration.

$$C = \frac{\text{DPM/ml} \times 128.2 \text{ } \mu\text{g}/\mu\text{mol}}{(2.2 \times 10^6) \text{ DPM}/\mu\text{Ci} \times 4.7 \text{ } \mu\text{Ci}/\mu\text{mol}} \quad (4.7)$$

5. The mass of naphthalene in solution (M_n , μg) was calculated by multiplying the concentration of naphthalene in solution by the volume of solution.

$$M_n = C \times (V_w + V_n) \quad (4.8)$$

6. The mass of naphthalene in the gas phase (M_g , μg) was calculated using a Henry's law constant of $3.6 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$ (EPA, 1979). This constant in unitless form was calculated to be 0.015.

$$M_g = C \times .015 \quad (4.9)$$

7. The mass of naphthalene adsorbed per gram soil (Γ , $\mu\text{g/g}$) was calculated by subtracting the mass in solution and the mass in the gas phase from the total mass naphthalene in the vial.

$$\Gamma = \frac{M_{nt} - (M_n + M_g)}{M_s} \quad (4.10)$$

8. This provides the data for a single point on an adsorption isotherm (Γ, C_e) where $C_e = C$ for equilibrium conditions. Also, data for use in an adsorption kinetic study (Γ, t) is calculated in the same manner where t is the time the sample was analyzed referenced to initiation of the kinetic experiment.

Similarly, desorption data were determined according to the following calculation procedure:

1. The mass of naphthalene in solution at the beginning of the desorption phase of an experiment (M_{n1} , μg) was calculated by mass balance. In most cases 2.5 mL of solution containing naphthalene were removed and replaced with naphthalene free solution.

$$M_{n1} = [(C_e)_{ads}][(V_w + V_n) - 2.5] \quad (4.11)$$

2. The solution concentration of naphthalene (C_e) after desorption was calculated from the LSC analytical data as described in step 4 above. Calculations for mass in the gas phase (M_a) also were as described in step 6 above.
3. The mass desorbed (M_d , μg) then was calculated by subtracting the sum of the mass of naphthalene in solution at the beginning of the desorption experiment (M_{n1}) and the mass of naphthalene in the gas phase (M_a) at the end of the desorption phase from the mass of naphthalene in solution at the end of the experiment (M_n).

$$M_d = M_n - (M_{n1} + M_a). \quad (4.12)$$

4. The mass of naphthalene adsorbed per gram soil after desorption equilibration (Γ , $\mu\text{g/g}$) was determined by subtracting the mass desorbed per gram of soil (M_d) from the mass adsorbed per gram soil prior to the start of the desorption experiments.

$$(\Gamma)_{des} = (\Gamma)_{ads} - \frac{M_d}{M_s}. \quad (4.13)$$

5. This provides data to describe a single point on a desorption isotherm (Γ, C_e), or for use in a desorption kinetic study (Γ, t).

Soils Characterizations

The following tests were performed to characterize the soils for this project:

1. grain size distribution;
2. cation exchange capacity;
3. clay mineralogy;
4. pH;
5. surface area;
6. organic carbon content;
7. specific volume.

Grain Size Distribution

For each soil, four 250 mL bottles were required; two for samples and two for blanks. Ten grams of soil were placed in the two sample

bottles, then all four bottles were filled to the 3/4 level with distilled water. Ten mL of a dispersing agent (Sodium meta-phosphate, 50 g P/L; and sodium carbonate, 20 g/L) were added to each bottle, and the bottles placed on a shaker table overnight. The contents of each bottle then were poured into a 1.0 L settling column through a 0.05 mm sieve. This served to eliminate the sand fraction. Sufficient water was added to bring the volume to 1.0 L. To assay the clay content, each column was inverted several times to mix the contents, and a stopwatch was started. The soil in the columns was allowed to settle for six hours and fourteen minutes. This time was taken from tabulated data based upon Stokes' Law of settling at room temperature. This allowed one to subsequently withdraw clay sized particles exclusively.

Weighing beakers were placed in a 110°C oven for one hour, cooled in a dessicator, and weighed. After the six hours and fourteen minutes settling time had elapsed, 25 mL of supernatant solution were pipetted from each column at a depth of 9 cm and placed into a preweighed beaker. After the liquid had been evaporated from these beakers, they were reweighed to determine the mass of clay particles contained within. The mass of clay in the 25 mL aliquot was determined by calculating the difference in mass between the sample containing soil and the blank. The concentration of clay in the entire sample then was calculated by dividing the mass of clay in the aliquot by 0.025.

In addition, the particles remaining on the 0.05 mm sieves were washed into preweighed beakers which were placed into a 110°C oven overnight to evaporate the liquid and dry the samples. The beakers then were cooled in a dessicator and reweighed. The samples retained on the 0.05 mm sieve represented the sand fraction of the soil. Subsequently,

these samples were further fractionated by dry sieving through a series of sieves.

Sieve #18	1.0 - 2.0mm	very coarse sand
Sieve #35	0.5 - 1.0mm	coarse sand
Sieve #60	0.25 - 0.5mm	medium sand
Sieve #150	0.10 - 0.25mm	fine sand
Pan	0.05 - 0.10mm	very fine sand

The fractions of soil retained on each sieve were weighed. The mass of silt in the sample was calculated by subtracting the mass of sand and mass of clay from the total mass of the sample.

Cation Exchange Capacity

A procedure similar to the ammonium saturation method (57-2) described by Chapman (1965) in Methods of Soils Analysis was used to determine the masses of extractable sodium, potassium, calcium and magnesium. The procedure described was curtailed after leaching the soil with ammonium acetate. Instead of using chemical assays for the required elements, atomic absorption spectrophotometry was used to determine their concentrations in the leachate.

Similarly, for extractable aluminum, a method (67-4) similar to one described by McLean (1965) in Methods of Soils Analysis was used to prepare the leachate for extractable aluminum. Once again, atomic absorption spectrophotometry was used to determine the concentration of aluminum in the leachate.

The cation exchange capacity, expressed as meq/100g, was determined by summing the extractable sodium, potassium, calcium, magnesium and aluminum concentrations.

Clay Mineralogy

Clay mineralogy was determined according to an X-ray diffraction method described in Crystal Structure of Clay Minerals and Their X-Ray Identification (1980, ed. Brindley and Brown).

Determination of Soil pH

The soil pH was determined by adding 20 mL distilled water to five grams of soil (particle sizes < 2.0 mm) in a beaker. The contents of the beaker were thoroughly mixed, and allowed to settle for 30 minutes. Subsequently, the pH was measured using a pH meter with a glass electrode.

Surface Area

Surface area determinations were made using the BET Quantisorb System. The method involves measuring the amount of nitrogen gas that adsorbs to the soil surface, and subsequently calculating the surface area of the soil knowing the surface area occupied by each adsorbed nitrogen molecule. The measurements were performed in accordance with the Quantisorb System's instruction manual. Surface area determinations were conducted for the four soil types using particle sizes less than 2.0 mm.

Organic Carbon

Organic carbon content for all soils using particle sizes less than 2.0 mm was determined using the Walkley-Black Method as described by Allison (1965), method 90-3 in Methods of Soils Analysis.

Specific Volume

The specific volume for each soil was determined by placing a weighed mass of each soil type into a 10 mL graduated cylinder. Water

then was added to the cylinder using a burette to bring the total volume to 10 mL. After allowing the soil to wet for one hour, water was added to readjust the level to 10 mL. In all cases, the water required after the one hour waiting period was negligible. The specific volume was determined as the difference between 10 mL and the volume of water required to fill the cylinder, divided by the mass of soil added to the cylinder.

In addition to the soil characterizations described above, an attempt was made to determine the zero point of charge of the soils using a procedure described by Schulthess and Sparks (1986). This procedure involved preparing samples of soils in aqueous solution at three different ionic strengths. The pH is varied by adding either acid or base. A plot of pH vs acid and base added for the three ionic strengths should show a common intersection of the three titration curves at the zero point of charge.

This procedure was used to determine the ZPC for the Charleston and Tinker soils, but no intersection was observed. A personal communication with one of the authors of the report revealed that many natural soils do not exhibit a zero point of charge as determined using this procedure. In some cases, particularly when soils have expandable clays and little organic material, there are not enough pH dependent charges on the soil surface for a ZPC to occur. In these cases, the structural or permanent charge is so dominating that the surface charge is essentially independent of pH. For the Charleston and Tinker soils, it was evident that the surface was negatively charged regardless of pH. No further testing for zero point of charge was planned, since it appeared that little or no useful information could be obtained.

Nonetheless, following the naphthalene equilibrium sorption studies, a zero point of charge determination was made for the Greenville soil in an effort to explain ambiguous sorption results. This soil, consisting primarily of non-expansive minerals, exhibited a zero point of charge. Further discussion on this topic is presented in the results and discussion section of this report.

Surfactant Characterizations

The surfactant characteristics of concern in this investigation include critical micelle concentrations, soil adsorption, clay particle dispersion, and contaminant release characteristics, as well as biodegradability and toxicity. These characteristics were explored and used to identify the most effective surfactants for use in the contaminant sorption studies. Before each of these characteristics is described, an explanation concerning solute sorbent contact times is presented.

Solute-Sorbent Contact Times

The preliminary surfactant screening studies concerning surfactant sorption and contaminant release both required that the soil and solution be in contact prior to analysis. Ideally, the period of contact time allowed should be sufficient to ensure the samples are at thermodynamic equilibrium. In this regard, various so-called "equilibration times" ranging from hours (Schwarzenbach and Westall, 1981) to several days (Lapoe, 1985) have been used to quantify the sorption of organic compounds on soils. Since no clear guidance was available in the literature, it would be desirable to conduct a kinetic study for each sorbent/sorbate/solution system to determine the proper equilibration times. However, because of the large number of surfactants and soils

used in this study, and the fact that these sorption characterizations were conducted only for screening purposes, a kinetic study for each soil/sorbate combination was not warranted. Instead, a "minimum contact time" (MCT) was determined for these characterization studies.

The MCT was determined considering the period of time the volume of water used in a batch experimental unit would be in contact with the mass of soil used in an aquifer system. For example, the contaminant release study was conducted with one gram of soil and approximately five mL of solution. Assuming a typical bulk soil density of 1.8 g/cm^3 , results in soil bulk volume of 0.555 cm^3 , or a cube of soil with sides equal to 0.822 cm . In an aquifer, a conservative estimate of groundwater velocity is 10^{-5} cm/s , or 8.64 cm/day . At this velocity, it would take approximately 0.95 days for 5 ml of water to completely pass through 1 gram of soil. This period, 0.95 days, was used as the MCT of the groundwater and the soil.

Use of this MCT did not ensure that equilibrium was attained. But, since the surfactants are in contact with the soils for a time that is representative of a groundwater system, and the time (MCT) is the same for all surfactants, an adequate comparison between the candidate surfactants could be made for this screening study of contaminant release.

Critical Micelle Concentrations

The CMCs of all surfactants and surfactant mixtures screened for this project were determined using a method described by Mukerjee and Mysels (1971). Because the CMC is defined as the intersection of the two linear portions of a surface tension versus log surfactant concentration plot, surface tension measurements were made using the Fisher

Autotensiometer for various surfactant concentrations. The raw data obtained were manipulated according to the tensiometer's instruction manual to determine the surface tension for each dilution.

A computerized statistical system (Statistical Analysis System, SAS) was used to determine the CMC. A model was developed to represent the two linear traces of the surface tension versus log surfactant concentration plot.

$$Y = (1 - Z)[\alpha_1 + \beta_1 X] + Z[\alpha_2 + \beta_2 X] \quad (4.14)$$

where

Y = surface tension (dynes/cm),

X = log percent surfactant concentration,

α_1 = Y intercept of the linear portion of the curve at surfactant concentrations below the CMC,

α_2 = Y intercept of the linear portion of the curve at surfactant concentrations greater than the CMC,

β_1 = slope of the linear portion of the curve at surfactant concentrations below the CMC,

β_2 = slope of the linear portion of the curve at surfactant concentrations greater than the CMC,

$Z = 0$ if the data point occurs at surfactant concentrations below the CMC, and 1 at surfactant concentrations above the CMC.

If the point (ϵ, ϕ) is defined as the intersection of the two linear traces, ϵ represents the surface tension at the CMC and ϕ represents the log of the CMC. Since (ϵ, ϕ) lies on both linear traces,

$$\epsilon = \alpha_1 + \beta_1 \phi = \alpha_2 + \beta_2 \phi$$

which implies

$$\alpha_1 = \epsilon - \beta_1 \phi$$

and

$$\alpha_2 = \epsilon - \beta_2 \phi .$$

Substituting these values for α_1 and α_2 into Equation 4.14 and rearranging yields

$$Y = \epsilon + (x - \phi)[(1-Z)(\beta_1) + Z(\beta_2)]. \quad (4.15)$$

This model was programmed using SAS and initial values for the parameters ϵ , ϕ , β_1 and β_2 were estimated from a plot of the data as required by the computer program. The program used linear regression to fit the model to the data and provided least square estimates for all four parameters along with their 95 percent interval estimates.

Surfactant Sorption Screening Study

A single point sorption study was conducted for each surfactant solution. After the surfactant type was selected for use in the naphthalene desorption studies, a complete equilibrium adsorption isotherm was developed for the selected surfactant.

Single Point Surfactant Sorption Study

The objective of this study was to determine the extent to which each surfactant would adsorb to soils. Solution concentrations of surfactants were determined from standard absorbance versus concentration curves developed using the Beckman ACTA CIII Spectrophotometer. All of the surfactants exhibited absorbance in the ultraviolet range and a standard curve was developed for each surfactant. Adsorption studies were conducted for all four soil types for all surfactants. In addition, two types of blanks were prepared; surfactant blanks and soil blanks. A surfactant blank contained no soil and was used to determine the surfactant concentration in solution in the absence of soil. The soil blank contained no surfactant and was used as a spectrophotometric absorbance blank to account for soil leachate.

All experimental units were prepared by placing approximately 5 grams of soil into 20 mL glass vials. Fifteen mL of a 0.5 percent surfactant solution were pipetted into the vial. The samples were capped and mixed on rotating tumblers for a period of four days, which more than exceeded the MCT calculated to be 1.17 days. Thereafter, an aliquot of the solution was removed and centrifuged in 5.0 mL vials at 7000 rpm for thirty minutes before the supernatant was assayed for surfactant concentration.

To determine the amount of surfactant that had adsorbed to the soil, reference was made to the surfactant blank. It was assumed that the difference in the concentration of surfactant in the sample and the blank was attributable to soil adsorption. The fraction of surfactant adsorbed was calculated by .

$$\text{Percent Adsorbed} = \frac{C_{sb} - C_s}{C_{sb}} \times 100\% \quad (4.16)$$

where

Percent Adsorbed = the percent of the original mass of surfactant that adsorbed to the soil,

C_{sb} = the concentration of surfactant determined from the surfactant blank,

C_s = the concentration of surfactant in the sample after soil contact.

Surfactant Sorption Isotherm

This study was conducted for the surfactant selected for use in the contaminant sorption studies. Experimental units were prepared using the Charleston soil. Whereas, the single point sorption study described above provided useful information for screening purposes, the objective

of this study was to develop a complete sorption isotherm for the range of surfactant concentrations of interest.

Twelve dilutions of the selected surfactant using 0.01M CaCl_2 electrolyte solution ranging from zero to 1.0 percent concentrations were prepared. Thirty-six 40 mL glass vials were used to prepare a twelve point isotherm. Five grams of soil were weighed into 24 of the vials before all 36 vials were sterilized using propylene oxide. Twenty-five mL of each surfactant dilution were pipetted into three vials, two with soil and one with no soil (a surfactant blank). These bottles were placed on the rotating tumbler for five days. From a surfactant adsorption kinetic study conducted prior to this isotherm study, it was determined that five days would be sufficient that the extent of sorption would be within 1.0 percent of its thermodynamic equilibrium position. The kinetic study is described under the title, "Kinetic Studies," in a subsequent section of this report.

After the samples were removed from the tumbler, the soils were allowed to settle for 24 hours. Five mL of the supernatant were transferred into 5.0 mL glass microvials which were centrifuged at 6000 rpm for thirty minutes. Approximately three mL of the supernatant were transferred into a cuvette for analysis using the Perkin-Elmer Luminescence Spectrometer. Initial attempts made to use the ACTA CIII UV-visible Spectrophotometer showed that the instrument did not have the sensitivity to adequately analyze the lower surfactant concentrations.

The samples were analyzed in the following manner:

1. The emission and excitation wavelengths were determined using the automatic wavelength scan feature of the spectrometer. The selected wavelengths were 279/557, respectively, with slit widths set to 5 nanometers.
2. The spectrometer was zeroed by inserting a cuvette with 0.01M CaCl_2 dilution water and depressing the "auto zero" key.

3. The instrument then was calibrated with a surfactant blank. This was accomplished by inserting a cuvette containing the surfactant blank into the instrument, entering the blank concentration on the keypad and depressing the "auto concentrate" key.
4. For each set of three samples (1 blank and 2 experimental samples) the two samples drawn from the vials containing soil were introduced into a cuvette to obtain a reading on the instrument. The two readings were averaged to yield one data point for the isotherm.
5. The amount of surfactant adsorbed was calculated by mass balance.
6. Steps 2 through 4 were repeated for each surfactant dilution.

The analyses were conducted using surfactant concentrations on a volume percent basis. To develop the isotherm, however, the percents surfactant were converted to masses using a specific gravity of 1.1 as reported by the manufacturers.

Clay Particle Dispersion

Initially, a reflectance method, such as that used with a turbidimeter, was used to attempt to determine concentrations of clay suspended in aqueous and surfactant solutions. However, this proved ineffective due to an inability to distinguish between the reflectance of the surfactant micelles and that of the soil. On this account, an absorbance method similar to one described by Benson (1985) for making bacteriological counts was evaluated. This is based on the premise that a culture of bacteria acts like a colloidal suspension which absorbs incident light. The amount of light absorbed is directly proportional to the concentration of cells. Since a suspension of colloidal clay is similar to a bacterial culture, this method was evaluated for use in this investigation.

To evaluate the absorbance method for suspended clay determinations, various concentrations of a clay suspension obtained from the

Charleston soil were prepared using distilled water. The mass of soil in each dilution was determined by taking a specified volume of each sample, evaporating the liquid in pre-weighed dishes, and weighing each dish after all the water had evaporated. Using these solutions with known clay particle concentrations, standard clay particle absorbance curves were prepared at wavelengths of 350, 400, 430, 460, 500, 550, and 570 nanometers. Absorbance curves were prepared at several wavelengths in the event a particular surfactant interfered, in which case alternative wavelengths showing no interference could be used. Because most of the surfactants absorb only in the ultraviolet range, and very little interference was detected with the clay absorbance in the visible range, the absorbance method utilizing the Acta CIII spectrophotometer in the visible range was used.

The objective of the clay particle dispersion experiment was to determine the extent to which each of the surfactants mobilized colloidal clay in a suspension as compared with a distilled water suspension of soil. This was accomplished by placing equal amounts of Charleston soil into twenty-two 20 mL glass vials. Fifteen mL of distilled water were added to one vial and 15 mL of each surfactant solution at a 0.5 percent concentration were added to the remaining 21 vials. The vials were capped and rotated on a tumbler for 48 hours. The soil then was allowed to settle for 24 hours, whereupon the supernatant was analyzed for clay particle concentration. The resulting suspended clay concentrations for the surfactant solutions were compared with the corresponding concentration for the distilled water solution.

Contaminant Release

To determine the extent to which each surfactant solubilizes naphthalene, an experiment was conducted utilizing the Charleston soil and a solution of 14 carbon-labeled naphthalene. Two types of blanks were prepared for this characterization study; naphthalene blanks and soil blanks. Four naphthalene blanks containing no soil or surfactant were prepared by adding 5.0 mL of 0.01M CaCl_2 electrolyte solution to a 5.0 mL microvial and spiking this solution with 0.2 mL of the naphthalene stock solution (although the microvials are called "5.0 mL microvials," they actually have a capacity of approximately 6.2 mL). Four samples were prepared so that two could be assayed immediately, while the other two were assayed along with the samples containing soil after the adsorption phase of this experiment. This was done to determine the mass of naphthalene initially spiked into the samples as well as to account for any losses not attributable to soil sorption. Two soil blanks were prepared that contained soil and naphthalene, but no surfactant. These samples were prepared to define the extent of naphthalene desorption in the absence of a surfactant. They served as the zero datum with which the effectiveness of the surfactants for mobilizing the contaminant was compared.

To determine the effectiveness of a surfactant for solubilizing adsorbed naphthalene, the experimental units were prepared by first adsorbing naphthalene to the soil. This was accomplished in the absence of any surfactants by weighing equal amounts of Charleston soil, approximately one gram, into 44 of the 5.0 mL microvials. The soil was sterilized and all 48 vials were assembled by adding 5.0 mL of dilution water, and then spiking each sample with 0.2 mL of the naphthalene stock

solution. These vials then were capped and placed on a rotating tumbler along with two of the naphthalene blanks and the two soil blanks. The two remaining naphthalene blanks were centrifuged immediately at 6000 rpm for 30 minutes before 1.0 mL of supernatant was micro-syringed from each vial and injected into 7.0 mL of a liquid scintillation cocktail which was assayed using the LSC. All remaining samples were tumbled for five days, which exceeds the MCT, before analyzing them as previously described for the two naphthalene blanks. The sorbed phase concentrations were determined by mass balance referencing the two naphthalene blanks that had been carried through the entire sorption protocol. The mass of naphthalene in these two blanks was 6.7 percent lower than the two blanks assayed immediately after sample preparation. This difference was not considered excessive and did not affect the outcome of the experiment.

For the desorption phase, an additional 1.5 mL was micro-syringed from each experimental unit, bringing the total volume removed from each vial to 2.5 mL. Since there was no need to continue the naphthalene blanks, 44 experimental units were processed further. This was accomplished by placing 2.5 mL of distilled water in each of the two soil blanks. For each of the 21 surfactants tested, 2.5 mL of a 1.0 percent surfactant solution was added to each of two vials. All samples then were returned to the tumbler for four days after which they were assayed for naphthalene concentration as described above. The observations associated with the two replicates of each surfactant type were averaged. The interpretation of the results of this experiment are discussed in the "Results and Discussion" chapter of this report.

Biodegradability and Toxicity

As discussed in the literature review, Chapter II, biodegradation and toxicity information is available from the surfactant manufacturers. Swisher (1987) provided additional information concerning these areas. Once the most appropriate surfactant was selected for use in the naphthalene sorption studies, these sources were referenced to ensure that the surfactant was adequately biodegradable and nontoxic.

Kinetic Studies

The primary purpose of the kinetic studies was to determine the time required for a soil/naphthalene mixture to closely approach thermodynamic equilibrium during both adsorption and desorption studies. This was required to insure that a vast majority of a soil's equilibrium sorption capacity was obtained before sorption samples were analyzed. Such studies were conducted for trichloroethylene (TCE), 1,4 dichlorobenzene (DCB) as well as naphthalene. Results obtained for TCE and DCB studies showed that these compounds were unsuitable for use as previously discussed. The following kinetic study protocol pertains only to naphthalene.

These studies were conducted for both adsorption and desorption of naphthalene for each of the four soil types. Initially, one hundred 5.0 mL microvials were used to prepare samples, 20 for each soil type and twenty blanks without soil. The experiment was conducted in the following manner:

1. Microvials were acid washed and 1.00 ± 0.01 gram of soil with particle sizes less than $250 \mu\text{m}$ was added to 80 vials (20 vials for each soil type). The mass of soil in each vial was recorded.
2. Five mL of distilled water containing 0.01M CaCl_2 were added to each vial using a Fisher automatic burette. Subsequently, these were spiked with 0.20 mL of the naphthalene stock solution using a microsyringe.

3. One sample from each of the four soil types and one blank were centrifuged immediately and analyzed using the LSC. These samples were used to determine naphthalene concentrations at the initiation of the adsorption study.
4. All remaining samples were placed on a rotating tumbler. Nine were sacrificed at various times after the experiment was initiated to determine the loss of naphthalene with time to define adsorption kinetics.
5. After the solution phase concentration of naphthalene remained relatively constant with time (i.e., there was no discernible difference in DPM for the samples assayed), the desorption phase of the experiment was initiated.
6. The ten remaining experimental units for each soil type and ten blanks were centrifuged and 1.0 mL of the supernatant withdrawn and analyzed for naphthalene concentration. Thereafter, an additional 1.5 mL was microsyringed from each vial and 2.5 mL of 0.01M CaCl_2 water was added to each vial. These experimental units were returned to the tumbler.
7. Once again, samples were sacrificed at various times and analyzed to determine the increase in the concentration of naphthalene to define the rate of desorption.

Upon completing these studies, it appeared that biodegradation may have occurred since an unusual response was noted for the Greenville soil. There was an initial rapid decrease in naphthalene solution concentration which remained relatively constant for approximately three days. Thereafter, an additional decrease occurred typical of a biodegradation response with an initial lag period. Consequently, the biodegradation studies previously discussed were conducted leading to the decision to sterilize the soils before conducting any further studies. All kinetic studies were repeated using sterilized soil with the exception of the adsorption kinetic studies conducted with the Charleston and California soils. Because these two adsorption studies gave consistent results, they were not repeated.

The DPM data obtained from the kinetic studies were converted to masses of naphthalene adsorbed or desorbed per gram of soil by methods

previously described. The (Γ, t) data were analyzed using the kinetic models to describe the sorption process. In this case Γ equals the mass naphthalene adsorbed per gram of soil during the adsorption kinetic study, and Γ' represents the mass of naphthalene desorbed from the soil per gram of soil for the desorption study. A plot of the observations showed an initial rapid rate of sorption followed by a slow rate of decrease as the extent of sorption increased. Because this response was of an exponential form, the empirical first order kinetic model described in Chapter II was used. The coefficients of correlation all were in excess of 0.97 when using this model, except for the Tinker soil which showed negligible sorption. The high correlation indicated that the selection of this model was appropriate.

$$\Gamma = a(1 - e^{-\beta t}) \quad \text{or} \quad \Gamma' = a'(1 - e^{-\beta' t}) \quad (4.17)$$

where

Γ (Γ') = mass naphthalene adsorbed (desorbed) to (from) the soil per gram of soil ($\mu\text{g/g}$),

t = time (hrs),

a (a') = an empirical parameter representing the equilibrium adsorption (desorption) capacity of the soil ($\mu\text{g/g}$),

β (β') = an empirical parameter related to the rate at which the system attains equilibrium (hrs^{-1}).

An initial estimate for a (or a') was obtained from a plot of the data, and an initial estimate for β (or β') was calculated using the estimated value of a (or a') in the model along with one set of observations.

Preliminary parameter estimates were used along with a SAS nonlinear regression program to fit the observations, giving least squares estimates for a and β (or a' and β').

The results of the statistical analysis procedure were used to determine the minimum contact time required for the equilibrium sorption

studies. Ideally, one would want to ensure that 100 percent of the equilibrium sorption capacity of the soil had been attained, but, according to the model, the amount of time to do so is infinite. Most sorption occurs rapidly with equilibrium approached very slowly in the later stages. For example, from the analysis of the Charleston adsorption data, $a = 1.8114$ and $\beta = 0.0076$ ($R^2 = 0.984$). Rearranging Equation 4.17 and solving for t yields

$$t = \frac{-\ln(1 - \Gamma/a)}{\beta} \quad (4.18)$$

Assuming 95 percent attainable of the equilibrium sorption capacity, $\Gamma/a = 0.95$, and using the values of a and β obtained above in Equation 4.18, one calculates an equilibration time, t , equal to 394 hours. If a Γ/a of 0.99 were assumed, an equilibration time of 605 hours is calculated. The additional 211 hours required to attain a 4.0 percent increase in sorption was considered excessive, particularly when considering the analytical error associated with the experimental program. Accordingly, a value of 95 percent was selected as a compromise between time and equilibrium sorption capacity, and was used to determine contact times for all equilibrium sorption experiments.

Equilibrium Sorption Studies

Experimental Procedure

Adsorption and desorption (surfactant-solubilization) isotherms for naphthalene and three soil types were developed. Isotherms were not prepared for the Tinker soil because the sorption kinetic study showed very little adsorption. The desorption studies for each soil were conducted using five different surfactant concentrations: (1) no

surfactant, (2) below the CMC, (3) at the CMC, (4) above the CMC, and (5) well above the CMC. For each soil type the following procedure was used:

1. Seventy microvials (experimental units) were prepared for the sorption studies (refer to Figure 4.3). Also, five 40 mL vials (vials A through E) were prepared to monitor pH and conductance of the various solutions. These vials were processed along with the microvials through the end of the experiment.
2. All vials were acid washed, and 1.00 ± 0.01 gram of soil was weighed into vials 1 through 50. The mass of soil was recorded to the tenth of a milligram. Five grams of soil were weighed into bottles A through D.
3. All vials were sterilized according to procedures previously described.
4. All experimental units were assembled in a contamination control hood. Five mL of autoclaved distilled water containing 0.01M calcium chloride was added to each vial while a 25 mL aliquot was added to bottles A through D.
5. Samples 1 through 70 then were spiked with naphthalene by microsyringing various volumes of the naphthalene stock solution into each vial. The volumes transferred and resulting approximate solution concentrations in the vials are shown below (see Figure 4.3).

Row 1 -	0.050 mL	93 $\mu\text{g/L}$
Row 2 -	0.125 mL	139 $\mu\text{g/L}$
Row 3 -	0.200 mL	370 $\mu\text{g/L}$
Row 4 -	0.275 mL	510 $\mu\text{g/L}$
Row 5 -	0.350 mL	650 $\mu\text{g/L}$

6. Immediately after the naphthalene stock solution was injected into each vial, the vial was capped with a screw cap and teflon-lined septa.
7. Samples 1 through 60 were placed on a rotating tumbler while samples 61 through 70 (Figure 4.3, column G) were centrifuged at 6000 rpm for thirty minutes and analyzed for naphthalene using the LSC. This analysis was performed to compare the amount of naphthalene in solution in blanks at the beginning of the experiment with those at the end of the experiment. A difference would indicate an unaccounted loss of naphthalene from the vial.
8. Vials 1 through 60 were mixed on rotating tumblers for a period determined from the naphthalene sorption kinetic experiments. As previously discussed, this time period was based on attaining a minimum of 95 percent of the soil's equilibrium sorption capacity.

	A		B		C		D		E		F		G	
1	1	2	11	12	21	22	31	32	41	42	51	52	61	62
2	3	4	13	14	23	24	33	34	43	44	53	54	63	64
3	5	6	15	16	25	26	35	36	45	46	55	56	65	66
4	7	8	17	18	27	28	37	38	47	48	57	58	67	68
5	9	10	19	20	29	30	39	40	49	50	59	60	69	70

A	B	C	D	E
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Figure 4.3. Samples Used in Equilibrium Sorption Studies

9. After the appropriate time period, all samples were removed from the tumbler, centrifuged at 6000 rpm for 30 minutes and placed in the contamination control hood.
10. For each sample, the screw cap and septum were removed, and one mL of supernatant removed using a microsyringe was wasted. This was done to rinse the syringe.
11. A second mL of supernatant was microsyringed into 7.0 mL of a liquid scintillation cocktail contained in a 20 mL scintillation vial. This scintillation vial was set aside for later analysis using the LSC.
12. For samples containing soil (samples 1 through 50), an additional 0.50 mL was microsyringed and wasted from the sample vial bringing the total volume removed to 2.50 mL. This volume was replaced with a naphthalene free solution. Referring to Figure 4.3, the replacement solutions shown below, all prepared with distilled water, 0.01M CaCl_2 and pH adjusted to approximate the soil pH, were used.

Column A and Vial A - No surfactant
Column B and Vial B - 0.01% surfactant
Column C and Vial C - 0.05% surfactant
Column D and Vial D - 0.25% surfactant
Column E and Vial E - 1.00% surfactant

(Vials A through E had 12.50 mL removed and replaced with surfactant solution)

13. After each vial had been refilled, it was immediately recapped and set aside until all sample vials had been similarly refilled. Sample vials 1 through 50 (plus A through E) then were returned to the rotating tumbler for the desorption phase of the experiment. Blanks (samples 51 through 60) were not carried through this part of the experiment.
14. Once the desorption experimental units had been placed on the tumbler, the samples obtained from the adsorption phase were analyzed using the LSC.
15. The desorption samples were allowed to remain on the rotating tumbler for 48 hours. For all soils, this insured that the soil was within 95 percent of its equilibrium desorption capacity.
16. Samples 1 through 50 then were removed from the tumbler, centrifuged and 1.0 mL of the supernatant was withdrawn and analyzed using the LSC as described above.
17. Vials A through E were analyzed for pH and specific conductance, to obtain values that were representative of the pH and specific conductance for each surfactant concentration used in the experiment. This was accomplished by allowing the soil to

settle for one hour before the pH of the supernatant was measured. Ten mL of the supernatant were removed and diluted to 100 mL with distilled water. The specific conductance of the resulting solution was measured.

Also, to check whether naphthalene had indeed adsorbed to the soil, an extraction was performed on three samples after the desorption study had concluded. For these, the aqueous solution was drained from the sample, and the vial was filled with liquid scintillation cocktail. Although not all of the aqueous solution could be removed in this manner, most of the interstitial water that remained would be removed during subsequent extractions, leaving negligible amounts of aqueous solution which may contain some naphthalene ultimately remaining. These samples were shaken, placed on the rotating tumblers for several hours, centrifuged, and the supernatant poured into a scintillation vial containing approximately 7.0 mL of fresh cocktail. The scintillation vials were analyzed using the LSC. This procedure was repeated three consecutive times for each sample, and the results used in a mass balance to account for all the naphthalene. For all soils, this resulted in an average accountability of greater than 90 percent of the naphthalene.

Data Analysis

The disintegrations per minute data obtained from the LSC analysis were converted into mass naphthalene adsorbed per gram soil, Γ , and equilibrium solution concentration naphthalene, C_e (mg/L), as described earlier. For the adsorption phase, a 5 point isotherm could be determined, with ten replicates at each point; i.e., the experimental units in each row of columns A through E of Figure 4.3 were replicates. To obtain the isotherm, the data pairs (Γ, C_e) were averaged for each row (columns A through E), and the 95% confidence interval calculated. The

five average (Γ, C_e) points were plotted and the results showed that the isotherm was linear. This observation agreed with the findings of other researchers who used similar experimental systems. Schwarzenbach and Westall (1981) used linear isotherms to describe sorption of nonpolar compounds on aquifer material, and Schellenberg *et al.* (1984) found linear sorption for chlorinated phenols on sediments and aquifer materials. Karickhoff (1984) reported linear isotherms for hydrophobic compounds adsorbing to sediments when concentrations were less than one-half their solubility or 10^{-5} molar, whichever was lower. For the naphthalene sorption study conducted, the greatest concentration used was 650 $\mu\text{g/L}$, or $5 \times 10^{-6}\text{M}$, and is well below one-half its aqueous solubility.

The five point isotherm was used to calculate the partition coefficient, K_d , using SAS according to the model

$$\Gamma = K_d(C_e). \quad (4.19)$$

The least squares regression line was plotted along with the 95% interval estimates for each data point. This isotherm subsequently was compared with isotherms generated in the desorption phase of the experiment.

For the desorption phase, 10 points were used to develop the isotherm (all ten samples in each column listed in Figure 4.3). Although the two experimental units of each row within each column were replicates at the outset of the adsorption study, the extent of adsorption differed somewhat. Consequently, the initial conditions at the beginning of the desorption study were not exact replicates. For this reason, the two units in each row within a column could not be considered to be replicates.

Using the ten (Γ, C_e) points calculated, the regression line and partition coefficients were determined using the linear model (Equation 4.19) shown above. The resulting linear regression and data points were plotted for comparison with the adsorption isotherm.

Column Studies

Experimental Procedure

The column apparatus is described followed by the procedures used to prepare the solutions and soils. This section concludes with the methods used to conduct a column run itself, where a "column run" is defined as an experiment involving two columns where one was to be eluted with water and the other with a surfactant solution.

Column Apparatus

The column apparatus is shown in Figure 4.4. Each lower case letter preceding a component description below corresponds to the component indicated by the same letter in Figure 4.4:

1. (a) a 10 liter plastic Nalgene^R dispenser containing distilled water with 0.01M calcium chloride;
2. (b) a ten liter glass aspirator bottle containing surfactant solution;
3. (c) ten liter glass aspirator bottle containing naphthalene solution;
4. (d) three way Omnifit^R valves (Ace Glass Company). The body is made of teflon and the device is rated to 50 psi. Valves allow selection of the desired solution;
5. (e) three way omnifit connector (Ace Glass Company). The body is made of teflon. It is used for splitting the flow from one line to two lines and for attachment of pressure gauges and sampling ports;
6. (f) a Fisher MCP 2500 4-channel peristaltic pump;
7. (g) pressure gauges (Ashcroft, 0 to 60 psi) for monitoring column influent pressures;

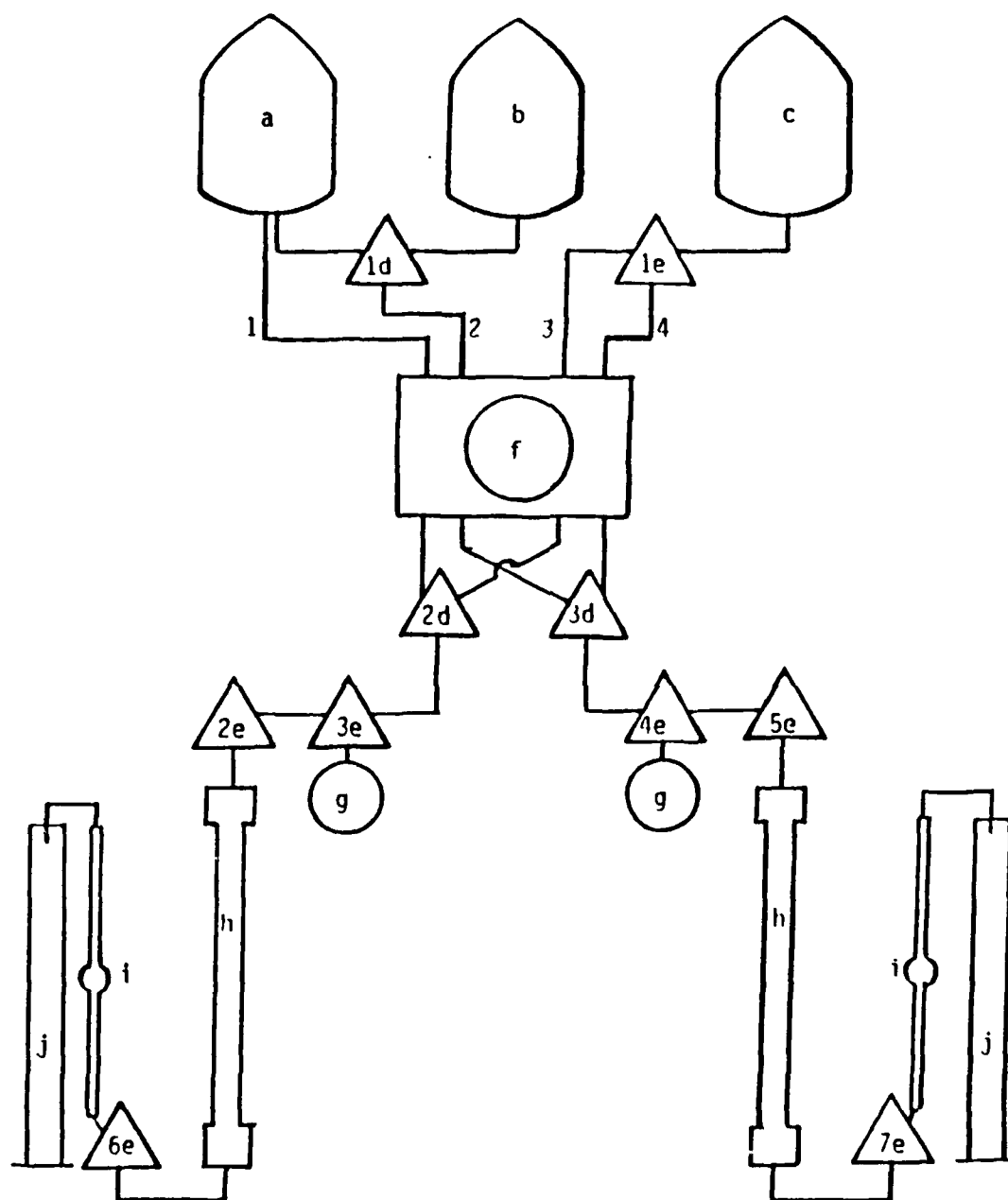


Figure 4.4. Schematic Diagram of Column Apparatus

8. (h) chromatography column. Adjusta-Chrom.[®] 2.5 cm I.D. by 300 mm glass with all teflon fittings from Ace Glass company. (The connectors adjacent to each column contained ports with septa allowing for influent and effluent sampling);
9. (i) two mL pipette. Allowed for a 3.0 mL sample to be taken from the effluent port; and
10. (j) one liter graduated cylinders.

Teflon tubing (0.8 mm I.D.) was used throughout with three exceptions: (1) the tubing immediately adjacent to each column was 1.6 mm teflon tubing; (2) lines that carried only water from the reservoir were tygon and C-Flex[®] tubing; and (3) the tubing that came into contact with the pump head was 1.6 mm I.D. tygon tubing. The latter exception caused the greatest concern since naphthalene and surfactant adsorbs to tygon tubing. Less reactive C-Flex[®] tubing was tried initially, but it developed leaks within a short period of time. The amount of tygon tubing was minimized by using it only within the pump head itself.

Solutions and Soils Preparations

Solutions

Originally, the use of ¹⁴carbon-labeled naphthalene was planned for preparing the naphthalene solution, however preliminary investigations showed that approximately 6.0 L of the solution would be required for each column run. Because this required the use of excessive amounts of labeled naphthalene, non-labeled naphthalene was substituted and the luminescence spectrophotometer used for analyzing concentrations.

Three different solutions were used for each column run; a prepared water solution, a naphthalene solution and a surfactant solution. To prepare the solutions, three six-liter volumetric flasks were filled with a 0.01M CaCl₂ electrolyte solution made with distilled water.

These flasks were autoclaved for 2.0 hours along with additional flasks containing distilled water. Because liquid was lost from the 6.0 L flasks during the autoclaving process, autoclaved distilled water was added to each flask to replace the lost water. This was accomplished prior to preparing the solutions used for the column run.

Since an aqueous solution with no surfactant or naphthalene was required to conduct a column run, the contents of one of the three flasks was poured directly into the 10 L plastic Nalgene[®] dispenser connected to the column apparatus. In the second flask, 60 mg of Fisher Certified Naphthalene crystals were added. This flask was placed on a heated magnetic stirrer, heated on low heat and stirred until all the naphthalene had solubilized which required approximately 24 hours. Approximately 230 mL of this solution were dispensed into a 240 mL amber bottle and capped with a Mininert[®] valve. This solution was used later to standardize the luminescence spectrophotometer when measuring naphthalene concentrations. The third flask was used to prepare the surfactant solution. This was achieved by adding 153.8 mL of the 10 percent surfactant stock solution to 6.0 L of water leading to the desired surfactant concentration of 0.25 percent. After preparation, the contents of the last two flasks were introduced to 10 L glass aspirator bottles for use in a column run.

Soils

The only soil used for all column runs was the Charleston Soil (particle sizes less than 2.00 mm). The soil was prepared in the following manner:

1. An approximate 1.5 kg mass of soil was removed from the soil container and a soil splitter was used to divide the soil into two equal parts. Each part was subsequently split repeatedly until each fraction contained slightly more than 75 g of soil.

2. Thereafter, 75.0 g quantities of soil obtained from each fraction were weighed into twenty 118 mL glass french mouth bottles.
3. Each sample was sterilized according to procedures previously described, except that cotton plugs were used instead of foam plugs because of the large size of the french mouth bottles. These samples were stored in a vent hood with the cotton plug inserted until used.

The soil was packed into the column according to the following procedures:

1. Each column was clamped upright with one endpiece installed on the bottom.
2. A long-necked funnel was inserted through the open end of the column.
3. A soil sample was removed from the vent hood, the cotton plug removed, and the plastic screw cap installed. The sample was rotated and shaken for approximately one minute to blend the soil.
4. The soil was poured from the french mouth bottle through the funnel. The funnel was lifted as the soil accumulated so that the funnel discharge always was approximately 1.0 cm above the top of the soil in the column.
5. The column was tapped 40 times using a wooden spoon to compact the soil particles.
6. The top endpiece then was inserted into the column, and the soil compressed to a depth of 10.9 cm.
7. Finally, the column was connected to the column apparatus such that influent solution would flow upward through the column. This was accomplished by removing the line between the column and the influent sampling port and rerouting it to the effluent sampling port (see Figure 4.4).

Conducting a Column Run

Once the solutions had been prepared and the soil packed into the columns, the column experiment could be initiated. Before describing the specific details of a column experiment, a brief description of the use of the pump and the luminescence spectrophotometer is presented.

Pump Operation

The Fisher MCP 2500 4-channel pump can pressurize four separate lines even though only two lines needed to be pressurized at any one time in these experiments. The pump was set up as shown in Figure 4.5. When soil in the column was being contacted with naphthalene during the adsorption phase, only lines 3 and 4 were used, whereas lines 1 and 2 were used whenever either water or surfactant solution were directed through the column. To switch from naphthalene to water/surfactant solutions, all four lines were momentarily pressurized, valves 2d and 3d adjusted, then lines 3 and 4 immediately depressurized. This minimized pressure surges to the system.

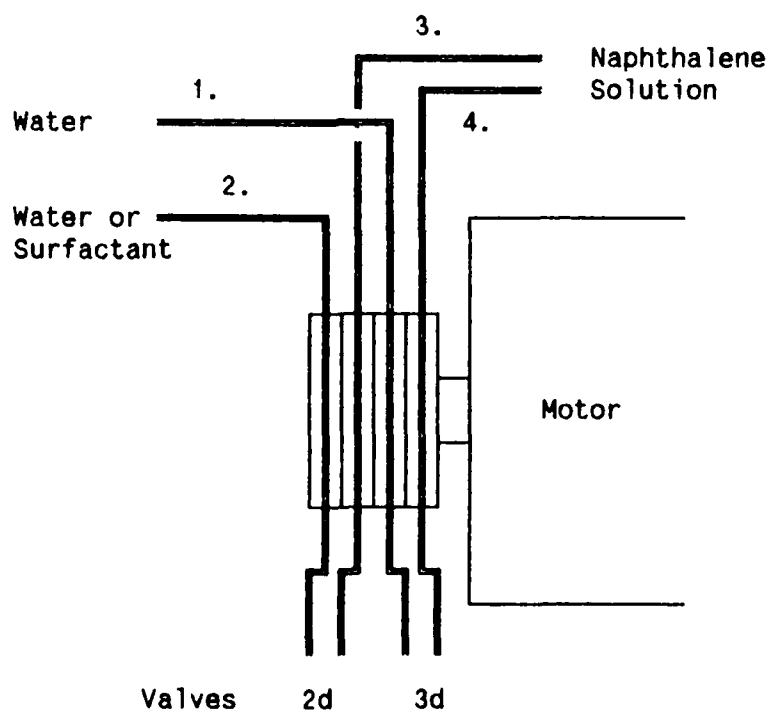


Figure 4.5. Pump Operation for Column Studies

Luminescence Spectrophotometer

Naphthalene concentration determinations were made using the luminescence spectrophotometer. Although wavelength scans showed that an excitation wavelength of 275 nm and an emission wavelength of 345 nm was optimum for naphthalene measurements, excessive interference from the surfactant was noted for these wavelengths. Consequently, excitation and emission wavelengths of 286 and 335 nm, respectively, were used with slit widths set at 5 nm. Under these conditions a minimal amount of interference was observed, less than 5.0 percent at the greatest surfactant concentration anticipated. This could be compensated.

To measure naphthalene concentration, the luminescence spectrophotometer was initialized by placing a cuvette containing a 0.01M CaCl_2 aqueous solution in the instrument and depressing the "auto zero" key. A sample then was syringed from the 240 mL amber bottle containing the prepared naphthalene solution, injected into a cuvette, and placed in the instrument. A value of 10.00 was entered on the keypad, and the "auto concentrate" key was depressed. A sample collected from the column apparatus then was placed in a cuvette and analyzed at wavelengths of 286/335 nm as well as 278/565 nm for the desorption phase of the experiment.

The second set of wavelengths listed above, 278/565 nm, was used to estimate surfactant concentrations in the effluent. This estimate was required to correct for surfactant interference with the naphthalene assay at wavelengths of 286/335 nm. Preliminary testing showed that a 0.25 percent surfactant concentration resulted in an apparent naphthalene concentration of 0.44 mg/L at wavelengths 286/335 nm. At wavelengths 278/565 nm, naphthalene did not fluoresce, and a 0.25 percent

surfactant concentration gave a reading of 0.23 when the instrument was standardized as explained above. Therefore, an estimate of the surfactant concentration was made at wavelengths 278/565, and this estimate was used to correct for surfactant interference at 286/335. The effluents of both columns were analyzed at both sets of wavelengths using the wavelength programming feature of the instrument. The concentration of naphthalene in the column eluted with surfactant was adjusted by

$$C_{\text{adjusted}} = C_{\text{read}} - [(S_{\text{ss}} - S_{\text{sw}}) \times (0.23/0.25\%) \times (0.25\%/0.44)]$$

where

C_{adjusted} = actual naphthalene effluent concentration,

C_{read} = naphthalene concentration read on spectrophotometer,

S_{ss} = spectrophotometer reading at wavelengths 278/565 nm on the column with surfactant wash,

S_{sw} = spectrophotometer reading at wavelengths 278/565 nm on the column with water wash.

Performing a Column Experiment

The following procedure was used for each of the column experiments (refer to Figure 4.4):

1. Each column was wetted by introducing the 0.01M CaCl_2 electrolyte solution in an up-flow mode, as previously described, through the column at 20 mL/h until approximately 80 mL had been discharged from the column. This was achieved by setting valves 1d, 2d and 3d for water flow.
2. The pump was turned off and the tubing rerouted for down-flow operation.
3. Down-flow of water was initiated by turning the pump on and introducing water at 20 mL/h. After several minutes, the rate was increased to 30 mL/h, then to 40 mL/h, etc. until a flow rate of 60 mL/h was established. The pressure associated with each flow rate was monitored and noted. This stepwise increase in flow to the final flow rates was required because preliminary column runs showed that an abrupt increase in flow rate would cause the soil to compact resulting in excessive pressures.

4. The flow of water was continued for several hours allowing the column to stabilize. Pressure variations were noted as soil particle rearrangement occurred within the column. A column was considered stable when the influent pressure to the column remained constant.
5. Once the column had stabilized, lines 3 and 4 were disconnected from valves 2d and 3d and placed into an open beaker. Both lines then were pressurized, bleeding air out of the lines and allowing naphthalene solution to flow freely into the beaker. After approximately 20 mL solution had been collected, each line was placed into a cuvette to collect a sample. Naphthalene concentration in the sample was measured using the spectrophotometer. In addition, the 1.0 L graduated cylinders (j) were emptied, and the volume discharged from the column was noted with time. These cylinders were used for the remainder of the experiment to monitor flow rates through the columns.
6. Lines 3 and 4 were depressurized, and reconnected to valves 2d and 3d. The influent was changed to naphthalene solution by pressurizing lines 3 and 4, adjusting valves 2d and 3d and depressurizing lines 1 and 2. Performing this in a rapid manner minimized pressure surges to the system.
7. After naphthalene solution began flowing into the column, samples were removed from the column using a syringe introduced through the effluent sample ports (6e and 7e). Approximately 3.0 mL samples were withdrawn for analysis. These samples were taken at various times throughout the run, and continued until the effluent concentration remained fairly constant. This indicated the conclusion of the naphthalene adsorption phase of the column run.
8. To initiate the desorption, or elution, phase of a column run, valve 1d was adjusted to allow surfactant solution to flow to column 2. Lines 1 and 2 were disconnected from valves 2d and 3d, and pressurized to remove air from the lines. These lines were subsequently depressurized and reconnected to the valves.
9. Because of concerns regarding pressure surges on the column, the next step depended on the elution flow rate required for a particular run. Since the flow rate was always 60 mL/h while soil in the column was saturated with naphthalene, whenever an elution flowrate greater than 60 mL/h was desired, the flow rate had to be increased gradually until the desired rate was attained. When the elution rate was 60 mL/h or less, pressure surges were not of concern and the appropriate rate was selected on the pump and the influent switched in the same manner as described in (6) above.
10. During the contaminant removal phase, samples were withdrawn from the effluent port at various times after elution began. This continued until only small concentrations of naphthalene (in most cases, less than 0.2 mg/L) remained in the effluent. In addition, the influent pressure was recorded to monitor changes induced by the surfactant wash.

11. At the end of each column run, the columns were prepared for the next experiment. They were disassembled and cleaned, all lines were washed with distilled water and line 2 from valve 1d to valve 2d was replaced with clean tygon tubing.

Analysis of Column Data

Naphthalene Loading

The data obtained while the column was loaded with naphthalene included time after the start of loading (t , hrs), naphthalene effluent concentration (C , mg/L) and volume eluted (V_e , mL). In addition, the dimensions of the soil column (L , cm; D , cm), mass of soil (M , gm) and specific volume of the soil (S_v , mL/gm) were required. The analysis followed the following steps:

1. The pore volume (p_v , mL) of the column was calculated.

$$p_v = \text{total column volume} - \text{volume of soil}$$

or

$$p_v = (\pi D^2/4)L - S_v(M). \quad (4.20)$$

2. The flow rate through the column (Q , ml/hr) was calculated.

$$Q = V_e/t. \quad (4.21)$$

(Note: V_e was adjusted from the volume read in the graduated cylinders by adding 3.0 mL for each effluent sample taken)

3. Time data were converted to number of pore volumes passed through the column (PV , unitless).

$$PV = (Q/p_v)t. \quad (4.22)$$

4. Effluent concentrations (C) versus number of pore volumes passed were plotted and noted to be "S-shaped"; i.e., in the shape of an ogive. The data were applied to a model describing a symmetrical ogive.

$$C = \frac{Q}{1 + \exp[\phi(\tau - N)]} \quad (4.23)$$

where

C = naphthalene concentration (mg/L),

N = number of pore volumes eluted (unitless),

Ω = parameter representing the maximum concentration of naphthalene discharged from the column after breakthrough (mg/L),

ϕ = parameter related to the dispersion within the column (unitless),

τ = parameter representing the number of pore volumes where the effluent concentration is one half of Ω (unitless).

The values of Ω , ϕ and τ were estimated from a plot of the data, and the model with estimates were programmed into a nonlinear SAS procedure which calculated least square estimates for these parameters. An advantage of using this particular model is that the parameter τ is an estimate of the retardation factor.

5. The data then were normalized by dividing the influent concentration of naphthalene (C_0 , mg/L). The value of C_0 was difficult to determine for these experiments primarily due to the pressure surges created when the influent port was sampled with a syringe. The influent pressure abruptly decreased followed by a rapid increase which caused the soil in the column to compress and the influent pressure to build-up. The pressures and compression were of an extent that these experiments had to be aborted. In order to avoid these adverse effects, it was decided that for subsequent experiments, only two readings of naphthalene influent concentration could be successfully obtained; one prior to connecting the naphthalene feed solution to the column, and the other after disconnecting the naphthalene feed from the column. The value of C_0 was taken as the average of these two concentrations. This was not ideal, however, as the actual influent concentrations varied somewhat from the beginning to the end of the experiment. Typically, the concentration increased slowly initially and then decreased toward the end of an experiment. This was attributed to two factors; adsorption of naphthalene onto the tygon tubing and volatilization of naphthalene in the 10 L glass reservoir. Further discussion on this particular topic is presented in the results and discussion section (Chapter V) of this report.

Naphthalene Elution

The data obtained from the desorption, or elution, phase of the experiment included naphthalene concentration versus time data as well as estimates for surfactant concentration for the columns eluted with surfactant. Steps 1 through 3 given above for the naphthalene

adsorption phase are applicable for this phase as well. After the naphthalene concentration for the column eluted with surfactant was corrected for interference as previously described, the data from both columns were normalized by dividing each observation by the value of C_0 determined from the adsorptive phase.

The normalized mass eluted was calculated by graphically integrating each normalized elution curve. Cumulative normalized mass eluted was calculated by first graphically integrating between the concentration versus number pore volumes (breakthrough) curve for the adsorption phase and a horizontal concentration line value equal to C_0 . This value, representing the amount of naphthalene adsorbed to the soil in units of PV·mg/L, could have been converted to mass by multiplying it by the number of liters per pore volume. However, because this conversion factor is canceled out in subsequent calculations of cumulative normalized mass eluted, the conversion was not made. The area under each effluent concentration versus number of pore volumes curve for the desorption phase then was calculated by graphical integration. Again, the units were PV·mg/L, and the value calculated for each step of the graphical integration was divided by the amount of naphthalene adsorbed to the soil calculated above. The units of PV·mg/L cancelled, leaving values of mass naphthalene eluted/mass naphthalene adsorbed (M_e/M_a). From a plot of this data for each column, comparisons could be made between masses eluted for the water and surfactant flushes at each flow rate, as well as among the columns for different flow rates.

CHAPTER V

RESULTS AND DISCUSSION

Preliminary Investigations

Soils Characteristics

A summary of the results of the soil characterization studies performed to categorize the four types of soil planned for use as sorbents is shown in Table 5.1. As discussed in Chapter IV, the pH varied among soil types. Stumm and Morgan (1981) reported that soil pH is typically in the range of 6 to 9. The pHs of the Charleston and Greenville, S.C., soils, would be considered to be low, California soil average and the Tinker soil very high.

The cation exchange capacity and surface area characteristics are highly dependent on the types of clays and minerals present. For example, montmorillonite is a highly expandable clay while vermiculite is a clay that has limited expansion. These minerals have high surface areas, and both have high cation exchange capacities with vermiculite exhibiting the greater of the two. On the other hand, kaolinite, illite and gibbsite are non-expansive, have relatively low surface areas, and low CECs. Another important difference among these minerals is that the three-layered clays, montmorillonite, vermiculite and illite, show little pH dependency of surface charge. Kaolinite and gibbsite both are materials which exhibit highly pH dependent surface charges (Bohn et al., 1985).

It is not surprising then that, based on the types of clays as well as the percent of clay in each soil type, the CECs and surface

Table 5.1. Summary of Soil Characterization Studies

SOIL	pH	SPECIFIC VOLUME (mL/g)	CATION EXCHANGE CAPACITY (meq/100g)	SURFACE AREA (m ² /g)	ORGANIC CARBON (%)	GRAIN SIZE DISTRIBUTION (%)							CLAY MINERALOGY
						VERY COARSE	COARSE	MEDIUM	FINE	VERY FINE	SILT	CLAY	
CHS	5.64	0.39	4.82	15.90	0.062	0.2	1.0	11.7	61.2	2.7	6.5	16.1	20% mont. 60% kaol. 10% illite
CAL	7.83	0.45	22.65	34.88	0.141	3.4	6.8	11.1	15.8	10.1	38.3	14.5	35% mont. 35% verm. 25% kaol.
GVL	5.89	0.49	0.31	5.40	0.060	20.3	18.2	12.3	13.0	6.7	19.2	9.4	50% gibbsite 40% kaol.
TIK	9.30	0.40	5.98	1.31	0.017	1.6	3.2	30.9	49.3	6.1	5.9	2.7	20% verm. 50% kaol. 25% illite

areas of the four soil types are as reported in Table 5.1. For example, the high CEC and surface area of the California soil can be attributed to the high clay content and large percentage of montmorillonite and vermiculite. Although the Charleston soil has a higher clay content than the California soil, it has a lesser amount of expandable clay, and therefore less surface area. Also, the Charleston soil contains no vermiculite, so its CEC is much lower. The low CEC and surface area of the Greenville soil can be attributed to the lack of expandable clays. The Tinker soil exhibits low surface area due to its low clay content. The CEC for this soil is higher than would be expected considering the low clay content. This could be due to the presence of gypsum (hydrated CaSO_4) in the soil (Smith, 1988).

The organic carbon content of all soils was fairly low, and it was anticipated that organic carbon content would not significantly influence sorption in these studies. Schwarzenbach and Westall (1981) reported that when the fraction of organic carbon exceeds 0.001 (0.1 percent), the extent of hydrophobic sorption is related to the amount of organic material present, whereas the mineralogy of the sorbent is more important for lesser amounts of organic material. The highest organic carbon content reported was 0.141 percent for the California soil; however, this is probably higher than actually was the case due to iron interference in the method of analysis.

Surfactant Characteristics

The results of the surfactant characterizations are summarized in Table 5.2. The last three characteristics shown, percent adsorbed to soil, percent clay dispersion effect and percent increase in contaminant

Table 5.2. Summary of Surfactant Characteristics and Interactions with Charleston Soil

Surfactant Number	Name	Type	Solubility	CMC (%)	Percent Adsorbed To Soil	Percent Clay Dispersion effect	% Increase in Contaminant Release Due to Surfactant
S-1	RP-710	Anionic	ADEQUATE	4.32	54.7	-100.0	908
S-2	Tween 60	Nonionic	ADEQUATE	0.012	94.1	55.7	311
S-3	Aerosol AY-65	Anionic	ADEQUATE	3.13	45.8	-100.0	361
S-4	Hamposyl C-30	Anionic	INADEQUATE	3.21	39.1	-100.0	340
S-5	Hamposyl L-30	Anionic	INADEQUATE	0.036	11.7	16.9	-102
S-6	Atlas G-2200	Anionic blend	INADEQUATE	7.31	75.8	-73.3	253
S-7	Igepal CO-630	Nonionic	ADEQUATE	0.004	95.7	73.6	245
S-8	Tween 20	Nonionic	ADEQUATE	0.006	76.8	27.5	131
S-9	BP-769	Anionic	ADEQUATE	6.22	57.0	-100.0	661
S-10	S-2 and S-8	Nonionic/nonionic	ADEQUATE	0.005	44.1	47.0	161
S-11	S-7 and S-8	Nonionic/nonionic	ADEQUATE	0.005	98.0	63.9	-32
S-12	S-5 and S-8	Nonionic/anionic	INADEQUATE	0.019	41.4	42.5	101
S-13	S-3 and S-8	Nonionic/anionic	ADEQUATE	0.024	40.3	-33.3	262
S-14	S-2 and S-7	Nonionic/nonionic	ADEQUATE	0.006	95.9	64.4	64
S-15	S-2 and S-1	Nonionic/anionic	INADEQUATE	0.065	59.4	-99.5	705
S-16	S-7 and S-1	Nonionic/anionic	ADEQUATE	0.007	60.2	-99.5	109
S-17	S-7 and S-4	Nonionic/anionic	INADEQUATE	0.004	67.6	-65.4	-7
S-18	S-7 and S-3	Nonionic/anionic	ADEQUATE	0.008	97.4	-98.1	99
S-19	S-1 and S-9	Anionic/Anionic	ADEQUATE	N/A*	53.4	-100.0	817
S-20	S-5 and S-3	Anionic/Anionic	INADEQUATE	0.124	65.4	-62.8	148
S-21	S-1 and S-4	Anionic/Anionic	ADEQUATE	.007	54.2	-40.5	78

*Not observed

release, were determined using the Charleston soil. Once again, this study was designed such that the surfactant selected for use in the naphthalene sorption study was to be based on the Charleston soil, and the surfactant ultimately selected for use employed for investigations conducted with all soil types. The underlined entries in Table 5.2 are explained in a following section entitled, "Surfactant Selection".

Solubility

Solubility appeared to be a concern only for some anionic surfactants or mixtures that contained anionic surfactants. Schwuger (1981) explained this phenomenon by relating that for many anionic surfactants, the presence of Ca^{2+} ions reduces solubility due to precipitation. Since precipitates within an aquifer would be detrimental to permeability, as well as remove much of the surfactant from solution, those surfactants that formed precipitates when added to a 0.01M CaCl_2 solution, were deemed inadequate; i.e., unsuitable for use.

Critical Micelle Concentrations

The CMC of each of the twenty-one surfactants and mixtures was determined as described in Chapter IV. For this project, the desired effect of surfactant addition is the solubilization of naphthalene. Since this requires the presence of micelles, the surfactant concentration at which micelles are formed is an important characteristic.

The nonionic surfactants showed much lower CMCs than anionic surfactants, supporting similar observations reported by Hall and Tiddy (1981). The measurements were made using distilled-deionized water as the prescribed procedure required (Mukerjee and Mysels, 1971). Had the determinations been made using the 0.01M CaCl_2 solution, the anionic

surfactants likely would have shown lower CMCs. In this regard, Hall and Tiddy (1981) reported that increased electrolyte concentrations decrease the amount of work required to overcome electrostatic repulsion among the negatively charged hydrophiles when micelles are formed.

The surfactant mixtures were of three different grouping types; nonionic-nonionic, nonionic-anionic and anionic-anionic. Generalizations concerning the CMC of these mixtures knowing the constituent surfactant's CMCs were formulated based on the category of mixture. For the nonionic-nonionic mixtures, all the CMCs were low and appeared to have values closer to that of the constituent surfactant with the lowest CMC. When nonionic and anionic surfactants were mixed, it appeared that micelle formation was initiated by the nonionic surfactant. The CMC of the 50:50 mixture appeared to be approximately twice the CMC of the nonionic surfactant; i.e., equivalent to the CMC of the nonionic surfactant. Also, the measured surface tension at the CMC of the mixture was near that of the nonionic surfactant. This indicates that the micelles that formed consisted primarily of the nonionic surfactant. The information listed in Table 5.3 demonstrates this relationship. For example, the CMC and corresponding surface tension for surfactant S-17 and its constituent nonionic surfactant, S-7, were exactly the same. This supports observations made by Cox *et. al.* (1985) who reported that, for a mixture of an ethylene oxide nonionic surfactant and linear alkane sulfonate (LAS), micelles were predominately formed from the nonionic molecules.

No generalizations for the anionic-anionic blends could be drawn. Only three different blends of this type were tested, and each showed a substantially different response. For S-19, a CMC was not discernible.

The S-20 mixture had a CMC similar to that of an anionic-nonionic blend, with the CMC closer to that of twice the lowest constituent CMC. For S-21, the CMC was reduced markedly from that of its constituents, showing a CMC more like that of a nonionic surfactant.

Clay Dispersion Effect

If a surfactant is to be successfully applied for an aquifer remediation project, it must not have deleterious effects on the permeability of the aquifer. Permeability changes may be caused by surfactant interactions with clay particles as noted by Ellis et al. (1985). Some surfactants cause clay particles associated with solid phases to become mobilized, while others cause mobile or suspended clay particles to coagulate. Either case leads to negative impacts on aquifer permeability or hydraulic conductivity.

A parameter termed the percent clay dispersion effect (PCDE) was developed to serve as an index of a surfactant's effect on the mobility of clay particles. The parameter is defined by the equation

$$PCDE = \frac{C_{cs} - 2021}{2021} \times 100\% \quad (5.1)$$

where C_{cs} is the concentration of clay in a surfactant solution and the value 2021 represents the experimentally determined clay concentration (mg/L) of Charleston soil in an aqueous solution of distilled water. If the clay concentration with the surfactant added to the solution was 2021 mg/L, then the surfactant was judged to have no effect on the dispersion of clay particles. The greater the extent to which the clay concentration differed from 2021 mg/L, the larger was the clay dispersion effect. A negative PCDE indicates that clay concentration in

solution was less with surfactant than without it indicating that the surfactant served to aggregate clay particles. For -100 percent PCDE the solution was entirely devoid of clay. Most of the anionic surfactants, with the exception of S-5, showed negative PCDEs, as indicated in Table 5.2. Most likely, the anionic surfactant served to destabilize and aggregate the colloidal clay particles leading to their removal from suspension.

All the nonionic surfactants showed positive PCDE values. A positive PCDE is indicative of an increase in clay concentration when compared with water alone. For the mixtures studied, all nonionic-nonionic blends showed positive PCDEs, while all anionic-anionic blends showed negative PCDEs. The nonionic-anionic blends all showed negative PCDEs with the exception of S-12. This particular surfactant includes the anionic surfactant S-5 which showed a positive PCDE when tested alone.

In conclusion, it appears that most surfactants and mixtures having an anionic component decrease solution clay concentrations. Also, surfactants and mixtures comprised solely of nonionic surfactants increase solution clay concentrations. These observations support Schick's (1986) observations that nonionic surfactants are considered anti-redeposition agents, as they cause little or no flocculation of clay slurries.

Surfactant Adsorption to Charleston Soil

Surfactant sorption studies were performed to compare the relative extents of sorption exhibited by the different surfactants and surfactant mixtures. Once again, minimal surfactant sorption to soils is desirable for any pump and treat application. From the data reported in

Table 5.2 several trends are evident. In general, the nonionic surfactants and mixtures composed of only nonionic surfactants showed the greatest extent of adsorption. This trend is related to the increase in clay particle dispersion discussed in the previous paragraph. Schick (1986) postulated that polyoxyethylene compounds are not only strongly adsorbed by montmorillonite but also remove the top layers due to their ability to intercalate between unit layers breaking up stacks. This phenomenon most likely occurs for the nonionic surfactants tested leading to the sorptive removal of the surfactant by mobilized and released clay particles.

In general, the anionic surfactants adsorbed to a lesser extent than did the nonionic surfactants; however, this observation may be an artifact of the screening protocol used. Only a single point sorption study was conducted for an initial surfactant concentration of 0.5 percent. For all nonionic surfactants and nonionic-nonionic mixtures, this concentration was well above the CMC of the surfactant. Above the CMC, surfactant sorption is near its maximum value (Louvisse and González, 1988; Lopota *et al.*, 1988). For most anionic surfactants tested, a concentration of 0.5 percent is below the CMC and may not be representative of the maximum amount of adsorption that would occur at higher concentrations. Even though a 0.5 percent concentration is above the CMC for the nonionic-anionic mixtures, the CMC is dictated primarily by the nonionic surfactant as previously discussed. It is possible that for some of these mixtures, most of the adsorption noted at the 0.5 percent concentration was due to the nonionic surfactant. The anionic co-surfactant might well show an increase in adsorption at higher concentrations. Then again, for some mixtures such as S-18, which showed a

97.4 percent adsorption level, nearly all of the anionic and nonionic surfactant were removed from solution. For nonionic-anionic mixtures in particular, processes and interactions are complex and generalizations cannot be drawn. Both increased surfactant adsorption (Schick, 1987; Somasundaran *et al.*, 1984) as well as decreased adsorption (Schwuger, 1981) have been reported for nonionic-anionic mixtures.

For anionic-anionic mixtures, adsorption did not appear to be affected substantially as compared with its constituent surfactants. For example, 53.4 percent of the mass of surfactant mixture S-19 was sorbed to the soil, while its constituents, S-1 and S-9, sorbed 54.7 and 57.0 percent, respectively. One additional observation worthy of mention concerns surfactant S-5. This surfactant appeared to be an exception in nearly all characteristics for an anionic surfactant. It had a relatively low CMC, a positive instead of negative PCDE, and, as will be seen, a negative contaminant release value. This particular surfactant, when used either alone or in a mixture, showed characteristics that were incongruent with the trends exhibited by other surfactants.

Contaminant Release

These experiments were conducted to compare the effectiveness of each surfactant to solubilize naphthalene adsorbed to the Charleston soil. As described in the previous chapter, soil and surfactant solutions were prepared using an 0.01M CaCl_2 electrolyte solution. This was important because naphthalene is expected to partition into surfactant micelles, and micelle formation is affected by the presence of electrolytes (Hall and Tiddy, 1981).

The solution concentration of surfactant added to each vial for the desorption phase of the experiment was 1.0 percent which resulted in an

approximate 0.5 percent surfactant concentration in the vial due to dilution. Although 0.5 percent was below the experimentally determined CMC for most of the anionic surfactants, the added electrolyte would have the effect of significantly reducing the CMC. Stellner and Scamehorn (1986) showed decreases in CMC on the order of 95 percent for anionic surfactants with addition of electrolytes. The fact that the anionic surfactants solubilized the naphthalene extremely well, as seen in Table 5.2, indicated that micelle formation had indeed occurred. Therefore, it appeared that, for this experiment, a 0.5 percent surfactant concentration was above the CMC for all surfactants and mixtures studied.

The values listed in Table 5.2 for contaminant release are relative to the desorption of naphthalene that occurred when no surfactant was added. For example, a 100 percent increase in contaminant release means that twice as much naphthalene desorbed in the presence of the surfactant than with water alone. A negative value indicates that less naphthalene was desorbed with surfactant present than with water alone. For the case of S-5 which showed a contaminant release of -102 percent, naphthalene actually adsorbed rather than desorbed after dilution with the surfactant solution. Occurrences of adsorption in the presence of surfactants have been reported by Scholze *et. al.* (1983) and Gaynor and Volk, (1976).

An arbitrary rating scale based on the range of solubilization performance was applied. The verbal descriptors used were "unacceptable", "fair", "good" and "excellent." An unacceptable rating was assigned to all surfactants that exhibited negative values of contaminant release. This was an obvious choice because the objective of using a surfactant

is to increase solubilization. An increase of solubilization of up to 100 percent was considered fair; 100 to 500 percent, good; and greater than 500 percent, excellent. Several observations were made using this rating scale. All the anionic surfactants showed good to excellent performance with the exception of S-5, which, as discussed previously, was found to be an exception in nearly every characteristic. All the nonionic surfactants were rated as good, but none solubilized naphthalene as well as did anionic surfactants. The nonionic-nonionic mixtures showed unacceptable to good performance, the nonionic-anionic blends ranged from unacceptable to excellent and the anionic-anionic mixtures were rated from fair to excellent.

Rickabaugh et al. (1987) used various surfactants and mixtures to aid in the removal of chlorinated hydrocarbons from surface soils. Results from batch tests indicated that a nonionic surfactant, ethoxylated nonylphenol similar to Tween 20 and Tween 80, removed the greatest amount of the contaminants. Subsequent column studies showed that a nonionic-cationic mixture produced the greatest contaminant reduction, followed by a nonionic surfactant and then an anionic-nonionic blend. These results differ from those described for this study in that anionic surfactants showed the greatest efficiency for removing naphthalene from aquifer material. It appears, therefore, that the types of contaminants as well as the characteristics of the soil are important considerations when selecting an appropriate surfactant for a particular application.

Surfactant Selection and Additional Testing

Surfactant Selection

The ideal surfactant for use in this investigation should be soluble, should not adsorb to the soil, have the same clay particle

dispersion characteristics as water, be an excellent solubilizing agent for naphthalene, and be nontoxic and biodegradable. An ideal surfactant could not be identified among the surfactants tested. Most likely one does not exist and trade-offs are necessary. For example, the surfactants that showed the best solubilization characteristics also were those that had the largest clay particle dispersion effects.

To select the most appropriate surfactant objectively, a systematic selection or screening procedure was developed. This encompassed the elimination of surfactants from consideration based on criteria established by the most objective means available. Working from left to right in Table 5.2, the characteristics considered were solubility, percent adsorbed to soil, percent clay dispersion effect and contaminant release. Many of the entries in Table 5.2 are underlined. The underline indicates that the surfactant related to the entry was eliminated from further consideration for use in this study because the particular entry exceeded the established standard. The standards and methods used to identify the most appropriate surfactant are presented below.

The first characteristic considered was solubility. It is not desirable to have precipitates form in an aquifer because precipitates undoubtedly have deleterious effects on permeability. In addition, precipitation removes the surfactant from solution thereby rendering it inactive as to its intended function of solubilizing the contaminant. Whenever a precipitate formed, the surfactant was deemed "inadequate" and removed from further consideration.

Excessive surfactant adsorption to soil was considered to be adsorption greater than one standard deviation above the mean of all surfactants tested. The mean was 63.2 percent and the standard deviation

was 22.9 resulting in elimination of all surfactants exhibiting adsorption levels greater than 86.2 percent of the mass of surfactant introduced to the batch equilibration system. Practically, this eliminated only those with adsorption levels greater than 90 percent.

Clay dispersion effects were considered in a manner similar to the way in which sorption effects were considered. Nonetheless, since both positive and negative effects had to be considered, the mean and standard deviation of the absolute value of the PCDE was determined. The mean was 69.7 percent with a standard deviation of 27.2 percent. Therefore, PCDE (percent clay dispersion effect) was considered excessive if the absolute value of the PCDE was greater than 96.9 percent.

With respect to contaminant release, all surfactants showing negative values were eliminated from consideration. This was an obvious choice as the objective of using a surfactant was to increase the solubilization of naphthalene.

After having applied the forgoing screening protocol, the only surfactants remaining for further consideration were S-8, S-10, S-13 and S-21. Of these four surfactants, S-13 showed the greatest contaminant release, the least adsorption to soil and the second most favorable PCDE. It clearly was the most appropriate of the four surfactants not previously eliminated. This surfactant, a 50:50 mixture of Tween 20 and Aerosol AY-65, was subjected to further testing to ensure its suitability for use.

Before these tests were conducted, however, a check on the toxicity and biodegradability of these two surfactants was performed. Swisher (1987) reported on two studies related to the biodegradation of Tween 20. These showed that Tween 20 was fully biodegraded in batch activated

sludge tests in one day and biodegraded at the 90-95 percent level in 20 days in a test described as "natural or synthetic medium inoculated with acclimated or unacclimated organisms." From the manufacturer's literature (ICI Americas Inc.), the acute oral LD₅₀ for rats for Tween 20 is reported to be above 38.9 grams per kilogram of body weight. The report states, "Relative to other materials, a single dose of this product is relatively harmless." For AY-65 the manufacturer's literature (American Cyanamid Company) states that this surfactant is completely biodegraded within two days using the Shake Culture Test. The acute oral LD₅₀ for rats was found to be 4.65 grams per kilogram body weight. Based on this information, it was concluded that these two surfactants should not be problematic with respect to biodegradability or toxicity.

Additional Tests Performed

Critical Micelle Concentration Under Varying Conditions

The objective of these tests was to determine how the CMC for surfactant S-13 was affected by changes in ionic strength and pH. To accomplish this, the CMC was determined using an 0.01M electrolyte solution for preparing the surfactant solutions. The pH of the resulting solution was adjusted to approximate the corresponding values of the Charleston and California soils. The CMCs determined under these sets of experimental conditions then were compared with the CMC determined earlier using distilled deionized water.

As described in Chapter IV, the model used to determine the CMC was

$$Y = \epsilon + (x - \phi)[(1 - Z)(\beta_1) + Z(\beta_2)] \quad (4.15)$$

where the statistical parameter ϕ represented the log percent surfactant concentration at the CMC. Data from the experiments are contained in

Appendix A and plots of surface tension vs log percent surfactant concentration data, along with the fitted model, are presented in Figure 5.1. The log percent surfactant concentration at the intersection of the linear portions of the plot represents the CMC. The results with distilled deionized water are shown in Figure 5.1(a). Figures 5.1(b) and 5.1(c) are similar but with increased ionic strength and at pH \approx 5 and pH \approx 7 respectively.

Using SAS the log percent surfactant concentration values representing the CMC and standard errors (Type 1 error rate = 0.05) are shown below.

Distilled-deionized water	$\phi = -1.75 \pm 0.36$
0.01M CaCl ₂ water, pH \approx 5	$\phi = -1.31 \pm 0.40$
0.01M CaCl ₂ water, pH \approx 7	$\phi = -1.10 \pm 0.94$

The interval estimates of the three values of ϕ overlap, and since the same model and number of data points were used for each data set, there is no statistical evidence to support the conclusion that there is a difference among the values of ϕ . It can be concluded that the CMC of this surfactant is not sensitive to the changes in ionic strength and pH used in these experiments. This indicates a stability which would be considered advantageous for a groundwater application.

A comment is required concerning the variability of pH for different dilutions of surfactant reported in Appendix A, particularly for the experiment where the samples were adjusted to pH \approx 7. Although the pH of these samples was adjusted prior to determining the surface tension, afterward the pH varied from pH = 5.35 for the 0.1 percent concentration to 7.28 for the 0.003 percent concentration. In addition, the measured pH values for concentrations greater than 0.1 percent increased with increasing surfactant concentration. The pH values reported in Appendix A

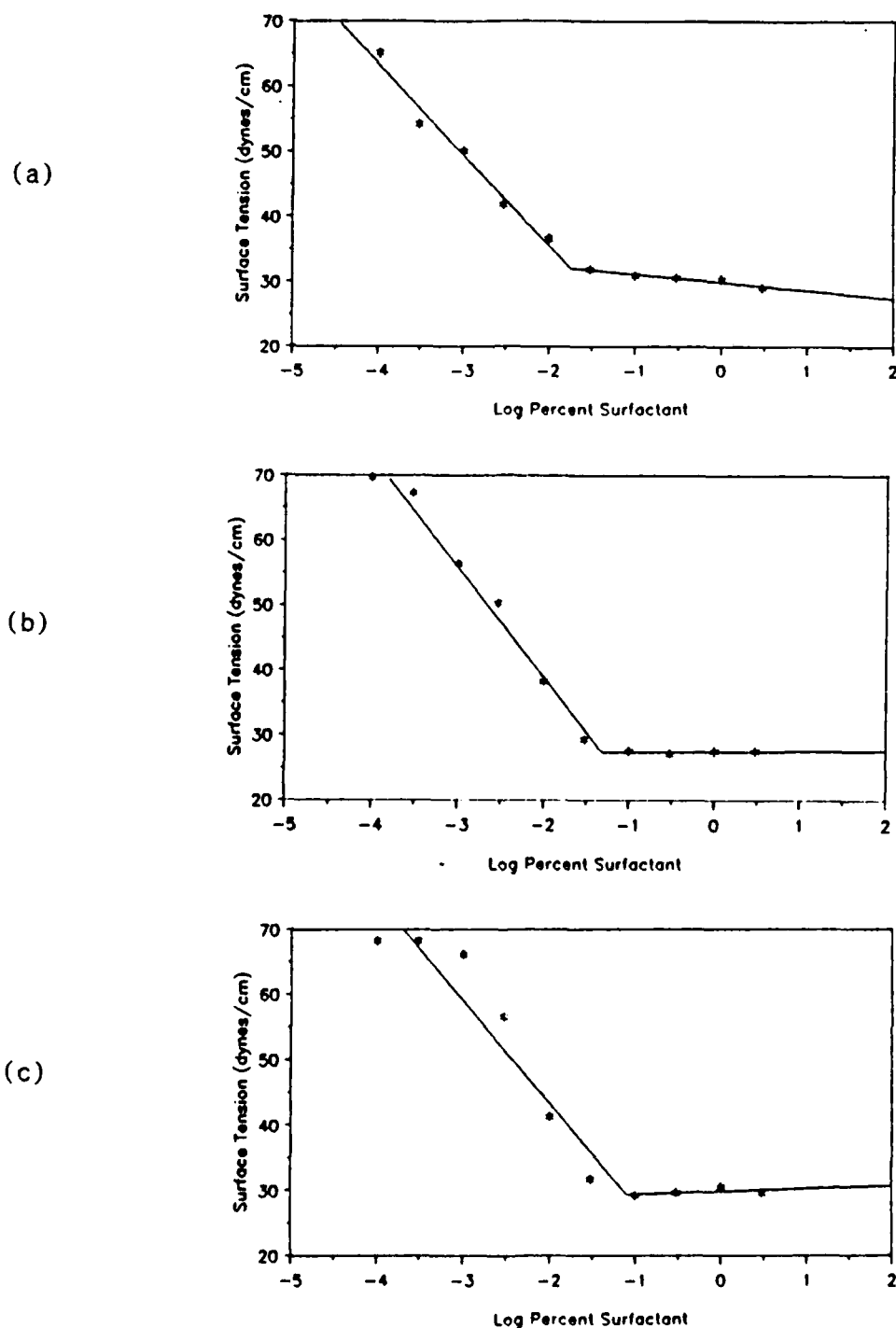


Figure 5.1. Surface Tension Measurements to Determine Critical Micelle Concentrations for Three Solution Conditions: (a) distilled deionized water, pH uncontrolled; (b) 0.01 M CaCl_2 in distilled water, pH adjusted to approximate Charleston soil; (c) 0.01 M CaCl_2 in distilled water, pH adjusted to approximate California soil

were measured several hours after the surface tension measurements were made and the samples had been exposed to the atmosphere. This delay and exposure to the atmosphere may have caused the pH to drift, however, it would not account for the unusual response where high and low surfactant concentrations resulted in high pH, whereas mid-range concentrations resulted in lower pH values. The reason for this unusual response could not be determined.

Surfactant Adsorption Isotherm

The single point sorption study conducted during the preliminary surfactant screening process provided limited information concerning the surfactant's extent of adsorption to Charleston soil. To more fully describe the adsorption process under conditions similar to those under which the naphthalene sorption studies were to be conducted, an adsorption isotherm was developed using the 0.01M CaCl_2 electrolyte for preparing the sorbate solution.

A plot of the results of the experiment are shown in Figure 5.2 with the data given in Appendix A. The solid lines connecting data points were included to show trends in the data. The initial portion of the curve appears to be linear until a point of sharp increase in adsorption is reached. The sharp increase occurs at the critical micelle concentration; i.e., 0.24 percent \approx 275 mg/L based on a specific gravity of 1.1. The shape of the isotherm is similar to that presented by Louvisse and González (1988) for Triton X-100, a nonionic surfactant. This indicates that adsorption of the nonionic surfactant predominated for the range of surfactant concentrations used for this study. The level of adsorption saturates above the CMC, although at about 3500-4000 mg/L

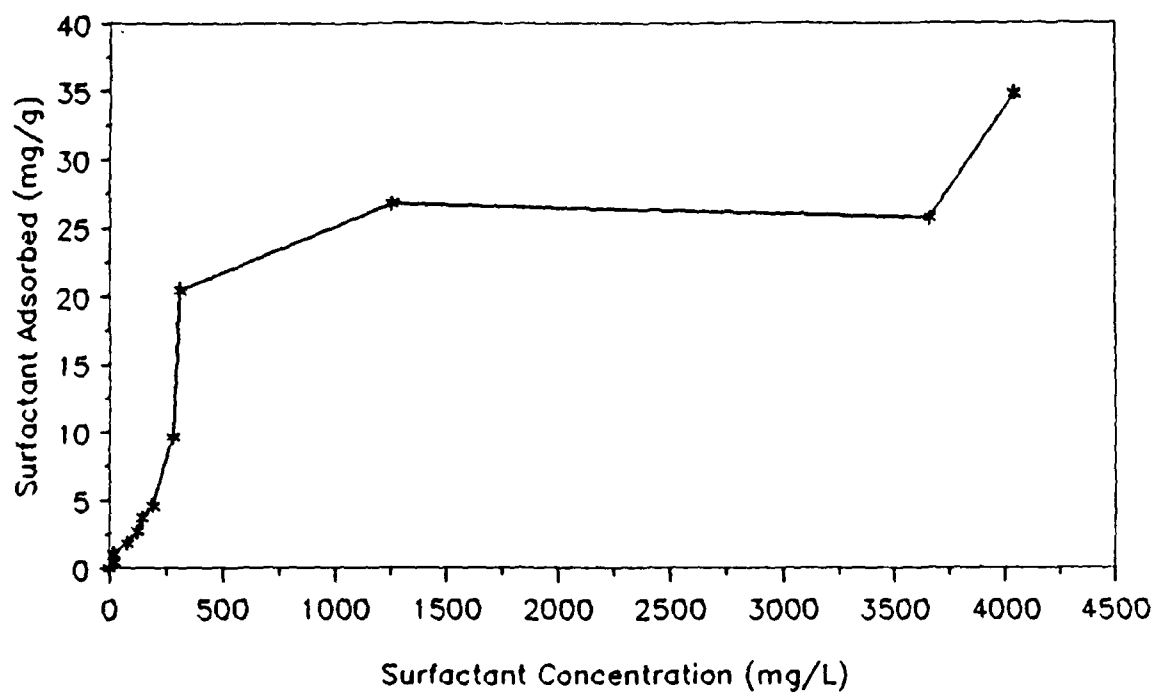


Figure 5.2 Adsorption Isotherm for Surfactant Tween 20/AY 65 Surfactant Mixture on Charleston Soil

it appears that it might increase once again. Although this latter rise could be due to experimental variability, it could also be due to the anionic surfactant forming hemi-micelles on the soil surface. With only one data point in this range, no judgements can be made as to whether this is actually an increase in adsorption or just data variability.

Neither the adsorption isotherm nor CMC tests under varying experimental conditions resulted in findings that would preclude the use of this surfactant for further investigation. Accordingly, this particular surfactant was selected for use in the naphthalene sorption studies. Henceforth, any reference to "the surfactant" refers to the mixture of Tween 20 and AY 65. The chemical structure of both surfactants are shown in Figure 5.3. Aerosol AY-65 is a sodium diamyl suffosuccinate and ionizes in solution with the Na^+ ion separating from the molecule. Tween 20 is a polyoxyethylene sorbitan monolaurate with the hydrophilic portion of the molecule consisting of 20 oxyethylene units, and the hydrophobic chain consisting of 12 CH_2 groups.

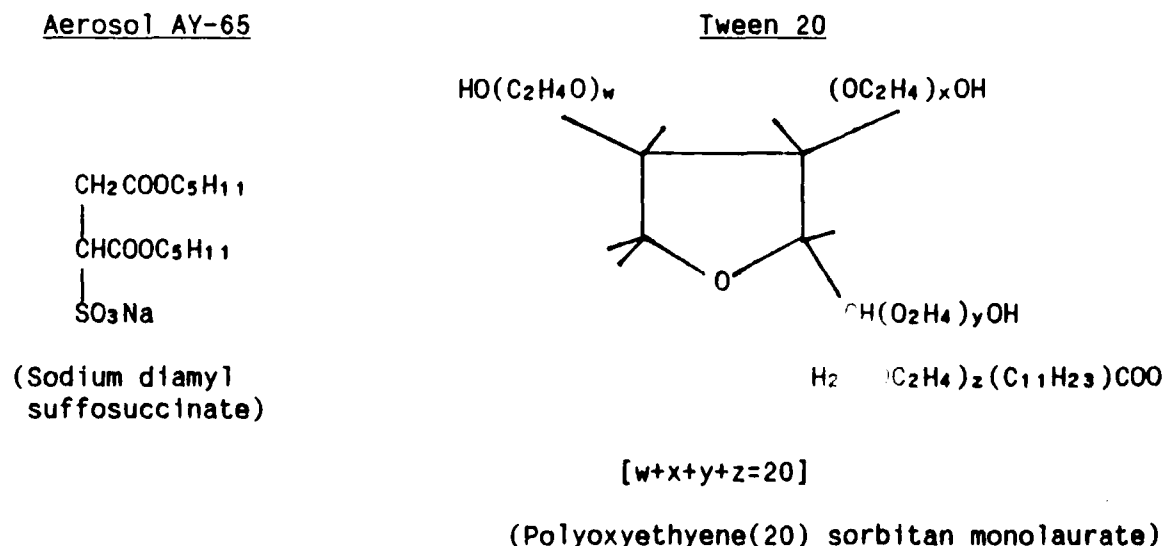


Figure 5.3. Chemical Structure of Aerosol AY-65 and Tween 20.

Kinetic Studies

Three types of kinetic studies were conducted. These studies included the rate of naphthalene adsorption onto the four soil types, the rate of naphthalene desorption from all four soil types, and the rate of surfactant adsorption onto the Charleston soil.

Rates of Naphthalene Adsorption

The kinetic responses of naphthalene adsorption onto the four soil types were modeled using the exponential model described in Chapter II.

$$\Gamma = a(1 - e^{-\beta t}) \quad (2.4)$$

where Γ is the mass of naphthalene adsorbed per gram of soil, t is the time in hours from the point of initiation of the experiment, and a and β are statistical parameters representing the equilibrium mass of naphthalene adsorbed per gram of soil and the rate at which equilibrium is attained, respectively. The lower the value of β , the longer it takes for the system to reach equilibrium. A summary of the results of the least squares regression analyses conducted on the observations for all soil types is presented in Table 5.4.

Table 5.4. Model Parameters and Results for Adsorption Kinetics of Naphthalene for Four Soil Types

Soil	a ($\mu\text{g/g}$)	β (h^{-1})	R^2	$T_{.95}$ (h)	Percent of Initial Mass of Naphthalene Adsorbed
Charleston	1.811	7.614×10^{-3}	0.984	394.0	87.8
California	1.156	3.750×10^{-2}	0.970	80.0	56.0
Greenville	0.362	3.750	0.983	0.8	17.5
Tinker	0.075	1.035×10^{-1}	0.825	28.8	3.7

A two-component model similar to one described by Wilczak (1988) utilizing two exponential terms, one for the initial rapid rate of sorption and a second exponential term for the subsequent very slow rates, was considered for use for this study. However, the analytical procedure used in these experiments was not sufficiently sensitive to detect the very slow sorption rates. Nonetheless, the high correlations (R^2) observed using the single exponential model (Equation 2.4), particularly for the Charleston, California and Greenville soils, indicated that the single exponential model used was appropriate.

The value of $T_{.95}$ was calculated using the model parameters according to the methods described in Chapter IV. It represents the time required to ensure that 95 percent of the soil's equilibrium sorption capacity had been attained. Figures 5.4 through 5.7 are graphical representations of the experimental observations and the fitted curves for the four soil types. The vertical and horizontal scales of these figures are identical to illustrate the differences among the soil types. Raw data and calculations are given in Appendix B.

The results of these experiments correlated with observations of Huang and Liao (1970) whose work involved determining the rates of pesticide adsorption onto clay minerals. They reported almost instantaneous adsorption onto kaolinite and illite with approximately equal capacity. However, for montmorillonite, a much higher capacity was noted with a two-phased kinetic response. The larger capacity was a result of increased surface area due to swelling. The first phase of the kinetic response for montmorillonite was almost instantaneous and was attributed to external adsorption. Because the second phase was much slower, the authors hypothesized a diffusion limited kinetic response.

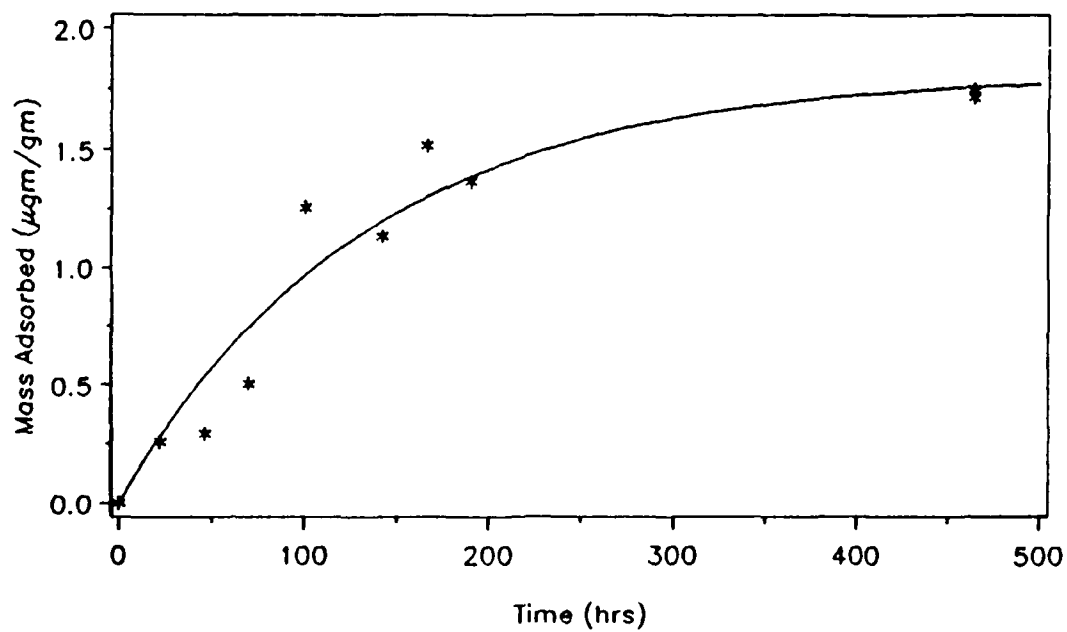


Figure 5.4. Rate of Adsorption of Naphthalene onto Charleston Soil

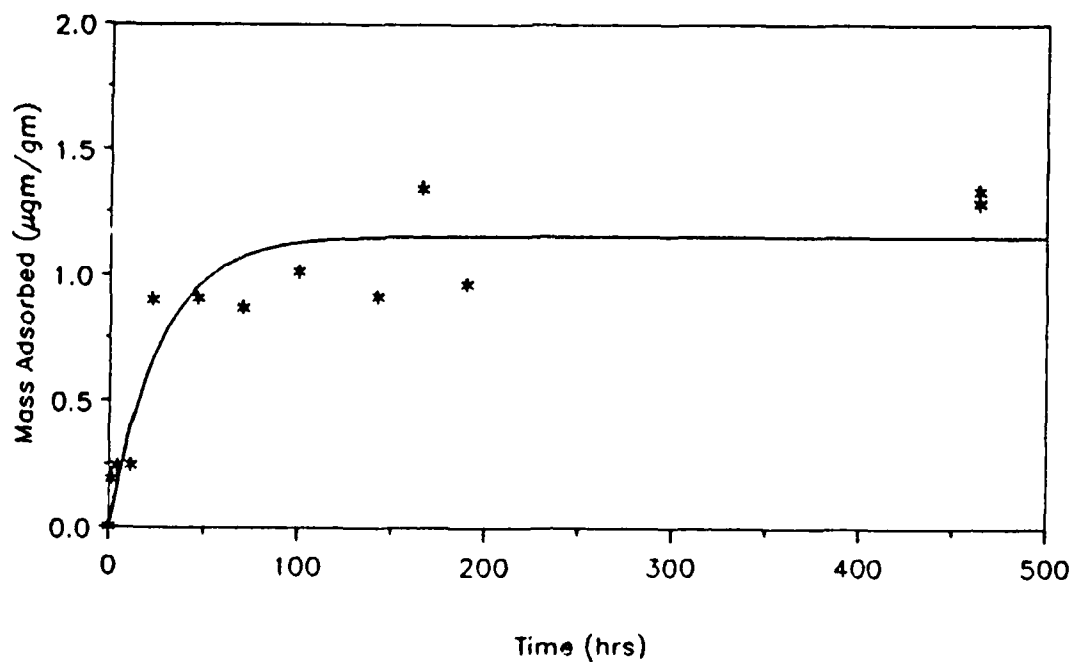


Figure 5.5. Rate of Adsorption of Naphthalene onto California Soil

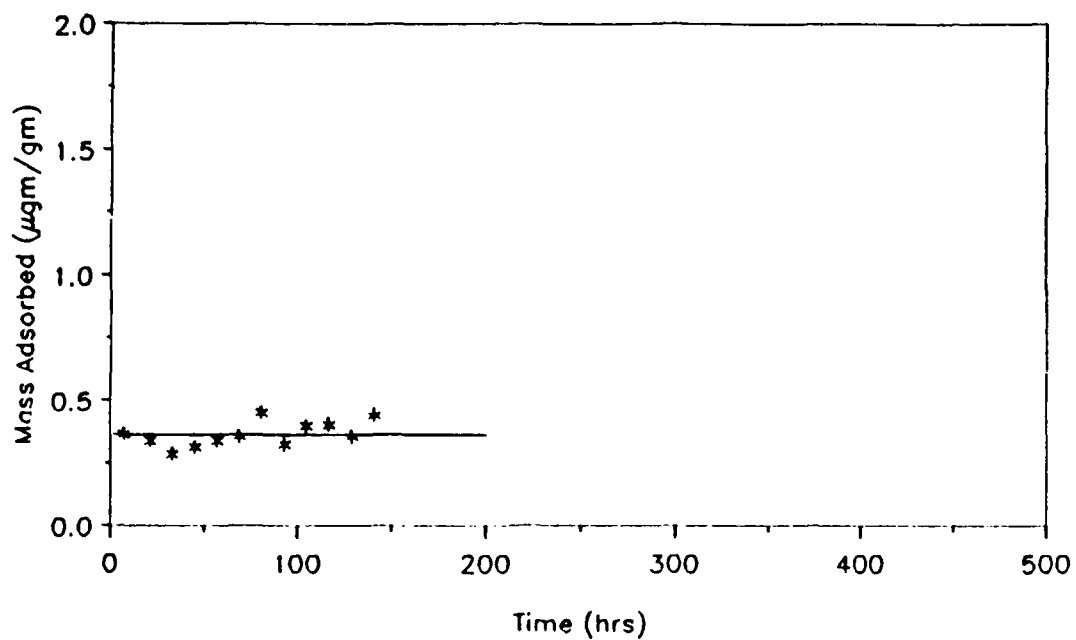


Figure 5.6. Rate of Adsorption of Naphthalene onto Greenville Soil

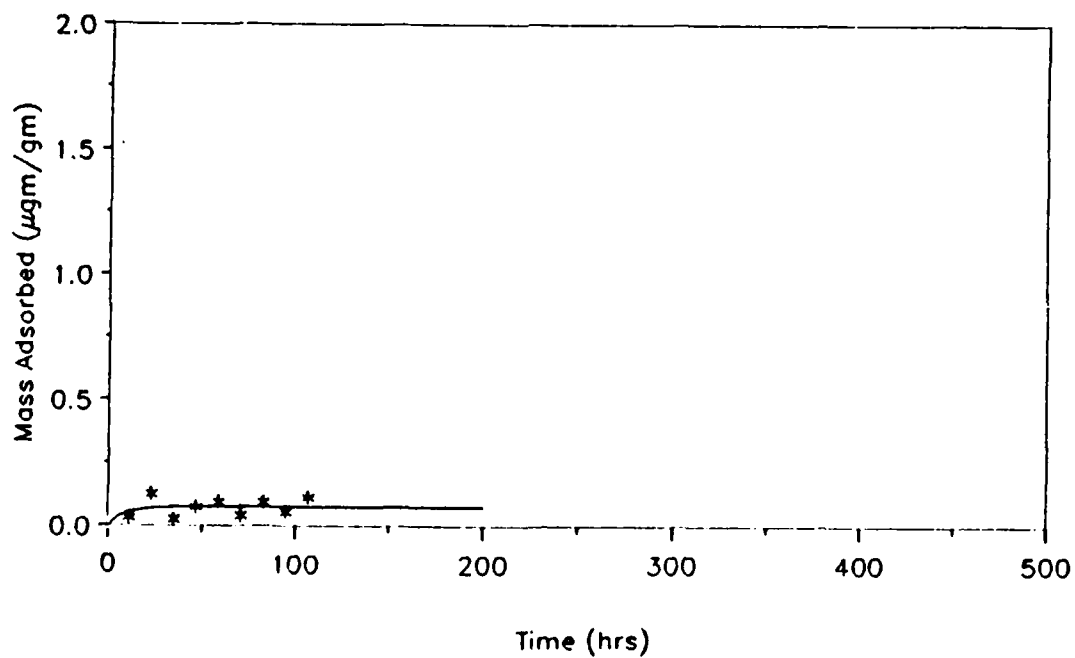


Figure 5.7. Rate of Adsorption of Naphthalene onto Tinker Soil

The Charleston soil showed the slowest approach to equilibrium with $\beta = 7.614 \times 10^{-3} \text{ hr}^{-1}$. A period of 394 hours was required to attain 95 percent of the soil's equilibrium sorption capacity. This length of time did not seem unreasonable, since Miller and Weber (1986) reported that "several days" were required to approach equilibrium for batch systems consisting of aquifer sands and aqueous solutions of nitrobenzene and lindane. Karickhoff (1984) reported that it may take several days to months for some systems to closely approach equilibrium. The clay mineralogical studies for the Charleston soil showed that it consisted of montmorillonite, kaolinite and illite. The adsorption seen during the initial phases of the experiment most likely is due to the adsorption of naphthalene to the kaolinite, illite and the outer surfaces of the montmorillonite. In the latter stages equilibrium is approached more slowly because the concentration gradient is decreased and naphthalene must diffuse between the clay layers of montmorillonite. Another factor which may have contributed to the reported response relates to the experimental procedure used. The soils were introduced into the reaction vials in a dry state before the solutions were added. Because montmorillonite swells in the presence of water, the observations reported most likely were affected by the rate of clay expansion. This would have the effect of reducing the apparent rate of naphthalene adsorption.

The parameter representing the equilibrium sorption capacity of the soil, α , was very high for the Charleston soil with a value of 1.811 $\mu\text{g/g}$ representing 87.8 percent of the mass of naphthalene initially introduced into the adsorption vial. This can be attributed to the large amount of surface area of the soil, 15.9 m^2/g , and to the relatively low

pH. Bohn et al. (1985) related that extents of adsorption are increased with increasing surface area, and Weber (1972) indicated that the adsorption of hydrophobic organic compounds increases as pH is decreased.

The California soil showed the next slowest approach to equilibrium, $\beta = 3.750 \times 10^{-2} \text{ hr}^{-1}$. Its clay fraction included montmorillonite, vermiculite and kaolinite. Because montmorillonite was present, an initial rapid rate of adsorption followed by a slow approach to equilibrium was expected. The surface area for this soil was determined to be 34.88 m^2/g and based on this alone, the California soil should have had a greater equilibrium adsorption capacity than the Charleston soil. This, however, was not the case in that α was equal to 1.156 $\mu\text{g}/\text{g}$ for the California soil. Two factors may have influenced this result: First, although vermiculite is an expandable clay, its expansion is very limited (Bohn et al., 1985) which implies that the internal surface area of this clay is not accessible for adsorption, particularly for molecules as large as naphthalene. Second, the pH of the California soil solution, $\text{pH} = 7.8$, was higher than that of the Charleston soil. As previously mentioned, in most cases an increase in pH results in a decrease in the adsorption of hydrophobic organic molecules. Both of these factors would serve to reduce the soil's equilibrium sorption capacity.

The Greenville soil, in contrast, consisted of kaolinite and gibbsite with no expandable clays. It appeared to attain equilibrium very rapidly, perhaps even before the first sample had been taken. To evaluate if this indeed was the case, a statistical test, the Principle of Conditional Error (Wilzcak, 1988), was conducted to determine whether there was evidence that equilibrium had not been attained by the time the first sample was collected. The method involved modeling the data

as a straight line for n_0 observations. Using the SAS for linear regression analysis, the slope and vertical intercept were estimated and the sum of squares error (SSE) on n_0-1 degrees of freedom (df) were calculated. The hypothesis that the slope of this line is zero, i.e., equilibrium is attained, is then tested by conditioning the model by setting the parametric condition that the slope of the line is zero. For this conditioned model, SAS determines an estimate for the vertical intercept along with the conditioned sum of squares error (CSSE) based on n_0-2 degrees of freedom. The sum of squares of the hypothesis (SSH) is equal to the difference between the CSSE and the SSE, and the f -statistic is calculated by

$$f_{1,(n_0-1)} = \frac{SSH/1}{SSE/(n_0-1)} \quad (5.2)$$

The hypothesis is rejected when the calculated f -statistic exceeds the critical value from the F -distribution with specified Type 1 error rate.

When this method was applied to observations obtained for the kinetic adsorption experiment conducted with the Greenville soil, the calculated f -statistic was 4.65. The critical tabulated F -value for a Type 1 error rate of 0.05 is $F_{1,10,.05} = 4.96$. Since $f_{1,10}$ is less than $F_{1,10,.05}$ the hypothesis is not rejected and it can be said that there is no evidence that the slope of the line is not zero leading one to conclude that equilibrium had been attained by the time the first observation was made; i.e., 7 hours after the experiment had been initiated.

The equilibrium sorption capacity, $a = 0.362 \mu\text{g/g}$, of the Greenville soil was much lower than that of both the Charleston or California soils. Since the pH of both the Charleston and Greenville soils was similar, the most likely reason for the difference in equilibrium

sorption capacities is that the surface area of the Greenville soil was comparatively low, $5.98 \text{ m}^2/\text{g}$, which can be attributed to the lack of expandable clays.

The Tinker soil's very low clay content of 2.7 percent consisted of vermiculite, kaolinite and illite. The fit of the kinetic model to the data obtained for the Tinker soil showed the lowest correlation of all the soils tested, $R^2 = 0.825$. Considering the low clay content, the presence of no expandable clays, and the small equilibrium adsorption capacity, the value reported for β , $1.035 \times 10^{-1} \text{ hr}^{-1}$, did not appear to reasonably represent the rate that equilibrium was attained for this soil. One would expect a more rapid approach to equilibrium. A statistical test similar to the one performed for the Greenville soil showed that, once again, there was no evidence that equilibrium had not been attained by the time the first data point was taken. Equilibrium, most likely, was attained at least as rapidly as for the Greenville soil. For both the Greenville and Tinker soils, there is likely a large degree of error associated with the values of β . When equilibrium is approached very rapidly, the value calculated for β is highly dependent on the time the first data point was taken as well as the magnitude of the concentration observed. If more data points were taken immediately after the outset of the experiment, a more reliable value of β could have been established. However, since the primary purpose of these experiments was to determine the amount of time required to contact the soil and solution for the equilibrium sorption studies, the results from these kinetic experiments were sufficient to establish those times even with less than reliable values of β . For the Tinker soil, the equilibrium adsorption capacity, $a = 0.075 \text{ } \mu\text{g/g}$, was very small, as would be expected based on the low clay content and high pH of the soil.

The results of these kinetic adsorption experiments can also be interpreted using the mathematical expressions presented for α and β in Chapter II. It was shown that

$$\alpha = \frac{k_a \Gamma_{\max} C_t}{k_a \Gamma_{\max} m + k_d} \quad (2.5)$$

and

$$\beta = k_a \Gamma_{\max} m + k_d . \quad (2.6)$$

For these experiments, the total amount of naphthalene in the reactor, represented by C_t , and the mass concentration of soil, m , were constant for all soils tested. The parameters that might vary among soil types were the adsorption and desorption rate constants, k_a and k_d , and the ultimate sorption capacity, Γ_{\max} , which is dependent on both the soil surface area and the pH of the soil.

From equation 2.5, it can be seen that when $k_d \ll k_a \Gamma_{\max} m$, α can be approximated by C_t/m , which means that almost all of the naphthalene will be adsorbed to the soil. For larger values of k_d , two effects are noted. First, the values of α decrease for larger values of k_d . Secondly, the value of Γ_{\max} influences the value of α . In this case, the amount of surface area available for adsorption as well as pH may be important factors when determining the extent of adsorption. The results of these experiments can be interpreted using this information.

For example, the Charleston soil showed a large extent of naphthalene adsorption. This indicates that the value of k_d is much lower than the value of $k_a \Gamma_{\max} m$. This could be a result of a large value for k_a , Γ_{\max} or both (m was held constant). As previously discussed, the Charleston soil had 15.9 m²/g of surface area, which is considerably more than either the Greenville or Tinker soils. It is most likely that

a high value of the sorption capacity of the soil would be associated with the large amount of surface area. The value of β for the Charleston soil, $7.614 \times 10^{-3} \text{ h}^{-1}$, was the lowest of all the soils, and Equation 2.6 shows that k_a must be small in order to have a low value for β , particularly for the Charleston soil where surface area, i.e., Γ_{\max} , was shown to be large. Therefore, for the Charleston soil, both k_a and k_d are expected to be small, and the higher sorption capacity is most likely due to the large amount of surface area available.

For the California soil, roughly half of the naphthalene in solution adsorbed to the soil, indicating that the value of k_d is not small compared with $k_a \Gamma_{\max} m$. Again, for this soil, the surface area was determined to be $34.88 \text{ m}^2/\text{g}$ which is more than twice that of the Charleston soil. However, this does not necessarily mean that the ultimate sorption capacity, Γ_{\max} , is more than twice that of the Charleston soil. As previously mentioned, much of the surface area may be inaccessible to the naphthalene and would have the effect of reducing Γ_{\max} . Therefore, faster desorption rates as well as a lower value of Γ_{\max} may have influenced the extent of naphthalene adsorption on the California soil, and resulted in a lower equilibrium sorption capacity when compared with the Charleston soil.

Both the Greenville and Tinker soils showed much lower equilibrium sorption capacities, q , than the Charleston and California soils. Analyses similar to those conducted for the Charleston and California soils provides the explanation for these observations. In both cases, the amount of surface area available is much less compared with the Charleston and California soils resulting in a lower Γ_{\max} . The higher values of β obtained for these soils, with reference to Equation 2.6, indicates

that the rate coefficients are most likely larger than the Charleston and California soils. Therefore, for the Greenville and Tinker soils, one would expect the fast rates of adsorption and the relatively low sorption capacities observed in these experiments.

These results concur with the results of other studies described in the literature. Katz and Uchrin (1986) conducted batch rate studies for the adsorption of the pesticide Lindane on sandy aquifer material containing a 4.0 percent organic fraction. Their study indicated that equilibrium was closely approached within 24 hours. Miller and Weber (1986) also studied the sorption of Lindane as well as nitrobenzene onto soils. Four soils were used ranging in organic carbon content from 0.10 to 1.14 percent. They found a rapid initial uptake of Lindane followed by a slower sustained rate requiring several days to approach equilibrium. The calculated first order rate constants for the responses of Lindane and nitrobenzene were 8.81×10^{-2} and $1.17 \times 10^{-1} \text{ hr}^{-1}$, respectively. These values are within the range of rate constants determined for naphthalene for this study. Rogers and McFarlane (1980) reported the rates of benzene sorption onto two silty clay loams and two types of montmorillonite. For all four soils, equilibrium was closely approached within 64 hours, which is within the range of values of T_{95} calculated for these experiments.

In summary, the equilibrium adsorption capacities as well as the rates of adsorption were affected by clay mineralogy and pH of the soil. Capacities correlated with clay content, with the soils having higher clay content exhibiting greater equilibrium adsorption capacities. The rates of adsorption were affected by the presence of expandable clays; i.e., those with expandable clays showed the slowest approach to

equilibrium. The effect that the organic carbon content of the soil might have had on adsorption capacities will be addressed following the the equilibrium sorption results in a subsequent section of this report.

Rates of Naphthalene Desorption

Analyses of the naphthalene desorption rate data obtained for all four soil types was conducted in a manner identical to that in which the adsorption kinetic data were analyzed. The similar model,

$$\Gamma' = a'(1 - e^{-\beta' t}), \quad (2.7)$$

was used to describe the rates of naphthalene desorption. In this case, however, Γ' represents the mass of naphthalene desorbed per gram of soil while a' represents the equilibrium mass of naphthalene desorbed from the soil per gram of soil. Consequently, the equilibrium sorption position for each soil type after the conclusion of the desorption step is calculated as the difference in the a value determined for the adsorption experiment and a' determined from the desorption experiment. The results of the analyses are summarized in Table 5.5 and graphical representations are shown in Figures 5.8 through 5.11. The raw data and calculations are given in Appendix C.

Table 5.5. Model Parameters and Results for Desorption Kinetics of Naphthalene from Four Soil Types

Soil	a ($\mu\text{g/g}$)	β (h^{-1})	R^2	$T_{.95}$ (h)
Charleston	0.170	0.187	0.986	3.7
California	0.168	0.331	0.995	9.1
Greenville	0.188	0.398	0.985	7.5
Tinker	N/A	N/A	N/A	N/A

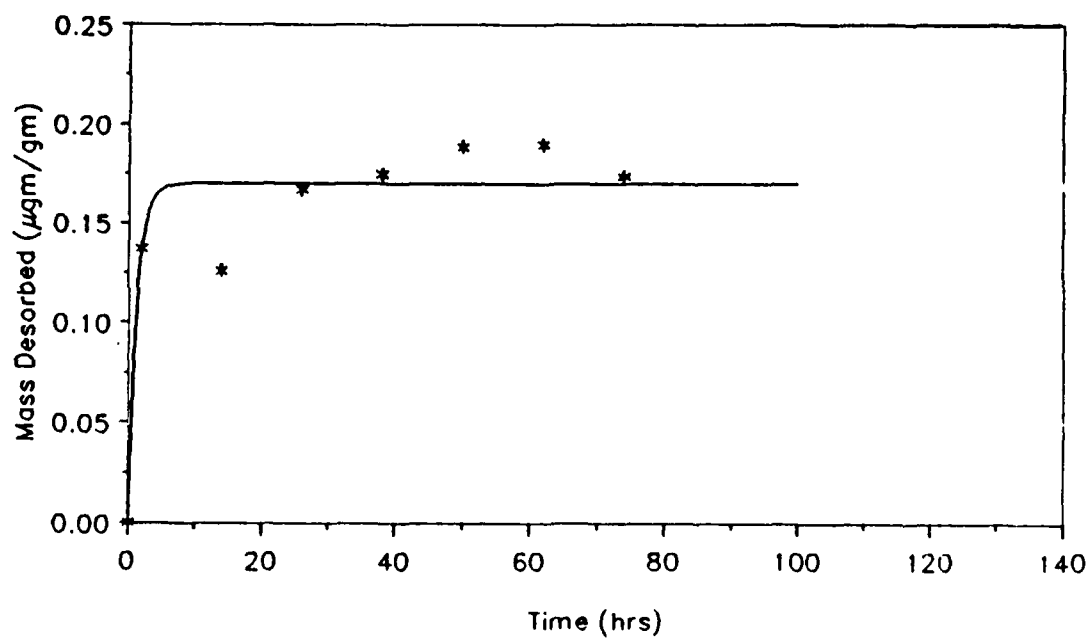


Figure 5.8. Rates of Naphthalene Desorption from Charleston Soil

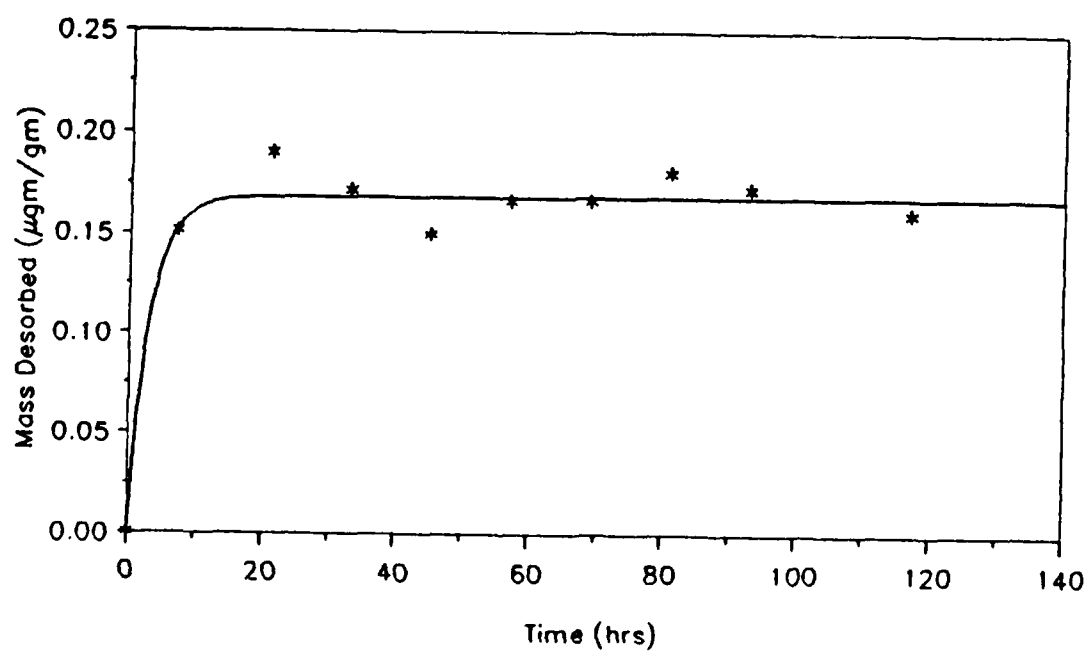


Figure 5.9. Rates of Naphthalene Desorption from California Soil

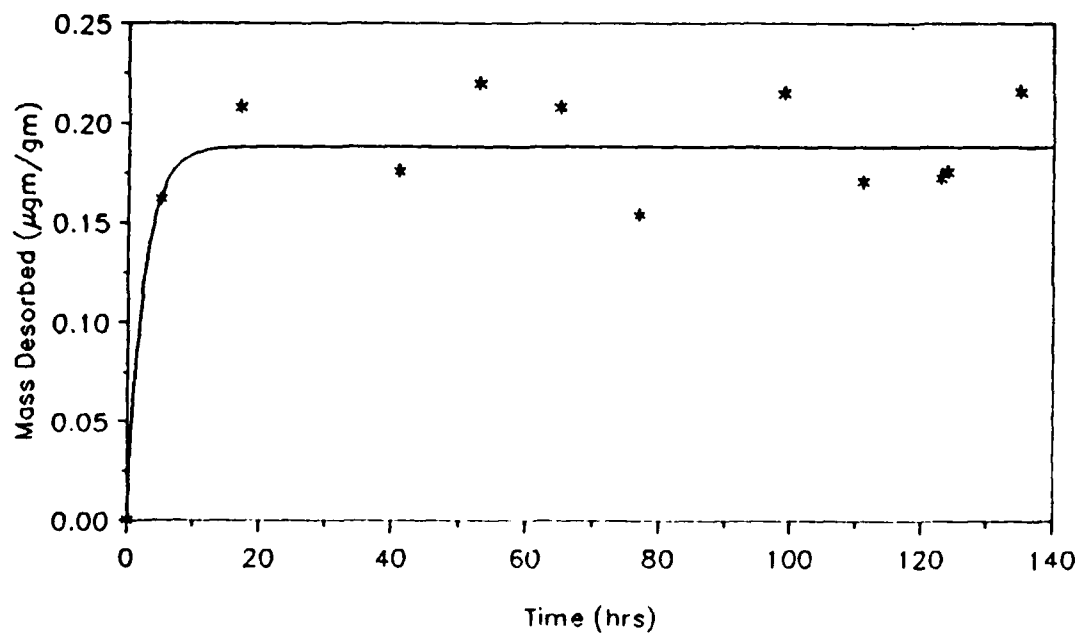


Figure 5.10. Rates of Naphthalene Desorption from Greenville Soil

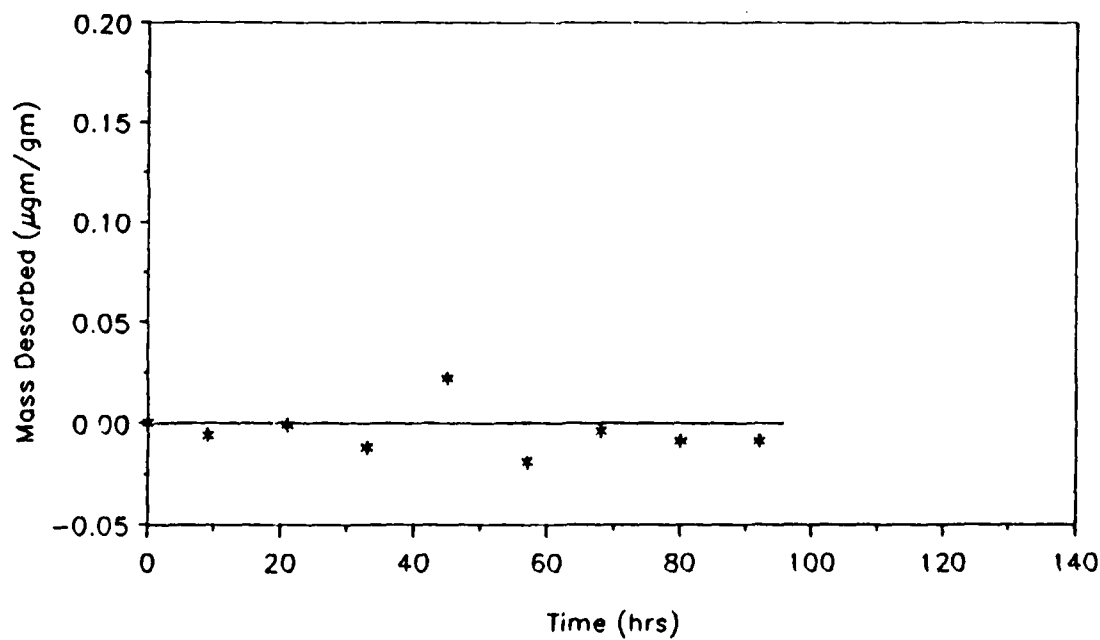


Figure 5.11. Rates of Naphthalene Desorption from Tinker Soil

The values of a for the California and Charleston soils are very similar even though the Charleston soil had adsorbed naphthalene to a greater extent during the adsorption phase of the experimental program. It appears that the Greenville soil with a value of $a = 0.188 \mu\text{g/g}$ desorbed more naphthalene than did either the Charleston or the California soils, even though much less had adsorbed onto the Greenville soil during the adsorption phase of the experiment. This apparent anomaly is due to the method used for diluting the experimental units when preparing them for the desorption experiments. For the Charleston and California soils, 2.5 mL of solution were removed and replaced to prepare them for the desorption experiments, whereas 4.0 mL were removed and replaced for both the Greenville and Tinker soils. This was done so that the extent of desorption would be sufficient to be able to analytically measure its occurrence for these two soils with lower equilibrium sorption capacities. The greater dilution of the Greenville soil resulted in a greater amount of naphthalene desorbed to attain equilibrium. For the Tinker soil, even with this increased dilution, no desorption of naphthalene was observed whatsoever. There most likely was a small extent of desorption, however, the method of analysis was not sufficiently sensitive to detect it. The solid line drawn on Figure 5.11 for the Tinker soil is not a statistically fitted curve, but rather a line referencing zero mass of naphthalene desorbed. The relative extent of desorption will be considered more thoroughly when addressing the desorption isotherm data.

The extent of adsorption for each soil type was consistent with the mathematical relationship described in the literature review for desorption.

$$a' = \Gamma_o \left[1 - \frac{\Gamma_o m}{C_{t0}} - \frac{f C_o}{C_{t0}} \right] \quad (2.8)$$

where Γ_o is the mass of naphthalene adsorbed at the conclusion of the adsorption kinetic experiment (a), C_{t0} is the total mass of naphthalene in the reactor for the desorption experiment, C_o is the mass of naphthalene in the solution phase at the conclusion of the adsorption experiment and f is the volume fraction of solution remaining after a portion of the solution was removed to dilute the sample in preparation for the desorption experiment. For example, approximate values for the Charleston soil are shown below.

$$\begin{aligned} \Gamma_o &= 1.8 \text{ } \mu\text{g/g} \\ m &= 1 \text{ g} \\ C_{t0} &= 2.1 \text{ } \mu\text{g} \\ f &= 0.52 \\ C_o &= 0.3 \text{ } \mu\text{g} \end{aligned}$$

Using these values and Equation 2.8 results in $a' = 0.12 \text{ } \mu\text{g/g}$, which compares favorably with the value of a' determined from the kinetic desorption study using the Charleston soil, $0.17 \text{ } \mu\text{g/g}$. The calculated values of a' for the other two soil types were also similar to the results obtained from the experimental observations (within a factor of 1.5) indicating the results from the desorption kinetic study were reasonable. However, the calculated values of a' were not consistently lower than the values determined from the experimental observations. For both the California and Greenville soils, the calculated values of a' were greater than the experimental values, indicating that no particular trend regarding the relative magnitudes of calculated and experimental values of a' was evident.

The rates of desorption for all soil types were similar with all values of T_{95} less than 10 hours. Particularly for the Charleston and

California soils, the rates of desorption were much greater than the corresponding rates of adsorption. The Charleston soil showed the largest difference in equilibration times between the rates of adsorption and desorption. Two factors may have influenced this. First, as compared with the adsorption study for which the soil initially was dry and the clay therein had to swell upon exposure to the solution, the clay had already been expanded at the outset of the desorption experiments allowing the naphthalene to diffuse outward more readily. Hence, the true rate of desorption may have been slower than the true rate of adsorption. But, the most significant factor influencing the rapid desorption rates observed most likely was that a portion of the naphthalene adsorbed was nonlabile. The rapid desorption rate observed, then, was for the labile fraction, and the method of analysis was not sufficiently sensitive to detect the slow desorption rate of the nonlabile fraction. This observation is supported by the fact that the relatively rapid rates of desorption observed in this investigation do not agree with some of the information available in the literature. Jaffe and Ferrara (1983) related that it is not uncommon for the rates of desorption reactions to be much slower than the rates of adsorption. Lapoe (1935) also found that the rates of desorption were much slower than the rates of adsorption for chlorinated hydrocarbons on a variety of soils, particularly for soils with high organic carbon content. In Chapter II it was shown that

$$\beta' = k_d \Gamma_{\max} + k_d \quad (2.9)$$

which shows that the rate constant from the adsorption kinetic experiment, β , and β' should be exactly the same. One would expect, then, that the kinetic rates would be either the same for the adsorption and

desorption experiments as predicted by Equation 2.9, or lower than the adsorption rate as reported in the literature. The rapid desorption rates, particularly for the Charleston soil, are also not consistent with the results of the adsorption kinetic experiment. This, again, supports the supposition that the rapid rates of desorption observed were due only to the desorption of the labile fraction.

The primary objective of conducting these studies was to determine an appropriate time to contact the soils and solutions for the naphthalene equilibrium desorption studies. Even though all the calculated values for $T_{.95}$ were less than ten hours, it was decided that a contact time of 48 hours be used. At the time that 48 hours was selected as the equilibration time, it was not recognized that this time period was based only on the desorption of the labile fraction. In retrospect, longer time periods should have been used to allow the nonlabile fraction to also closely approach equilibrium.

The Tinker soil showed essentially negligible sorption of naphthalene. Since the purpose of this study was to investigate desorption of naphthalene in the presence of surfactants, no useful information could be obtained using this soil as a sorbent. Consequently, the Tinker soil was eliminated from further study, and only the Charleston, California and Greenville soils were used for the naphthalene equilibrium sorption studies.

Rates of Surfactant Adsorption

The kinetics of surfactant (Tween-20/AY-65) adsorption to the Charleston soil were investigated for the primary purpose of identifying the appropriate contact time to use for developing the surfactant

adsorption isotherm. This isotherm was presented previously under the section entitled, "Surfactant Selection and Additional Testing." A second reason for conducting this experiment concerned the naphthalene equilibrium desorption isotherms to be conducted in the presence of the surfactant. As described in the previous section, the rates of naphthalene desorption were studied without surfactant present. However, since naphthalene desorption studies were to be conducted in the presence of surfactant, it was desired that the selected contact time for the naphthalene desorption studies, 48 hrs, be long enough to ensure a minimum of 95 percent of the soils equilibrium sorption capacity for both the surfactant as well as for the naphthalene.

This surfactant adsorption rate study was conducted in a manner similar to the one used for naphthalene, except that 40 mL bottles were used instead of 5.0 mL vials. This was done because surfactant concentrations were assayed using the fluorescence spectrometer and larger volumes were required for analysis. A soil:solution ratio of 1:5 was used in this kinetic study as it was for the naphthalene sorption study.

The experimental observations obtained from this sorption rate study were modeled using the same exponential model described previously for the naphthalene kinetic studies. The model constants were $\alpha = 26.02$ mg/g and $\beta = 0.368 \text{ hr}^{-1}$ ($R^2 = 0.998$). The observations and fitted curve are shown in Figure 5.12. The rate of surfactant adsorption appears to be rapid and, based on the model, the $T_{.95}$ for this surfactant was determined to be 8.15 hours. At 48 hours, the contact time planned for the naphthalene desorption studies with surfactant, it was calculated that more than 99.9 percent of the equilibrium soil adsorption capacity for surfactant would have taken place.

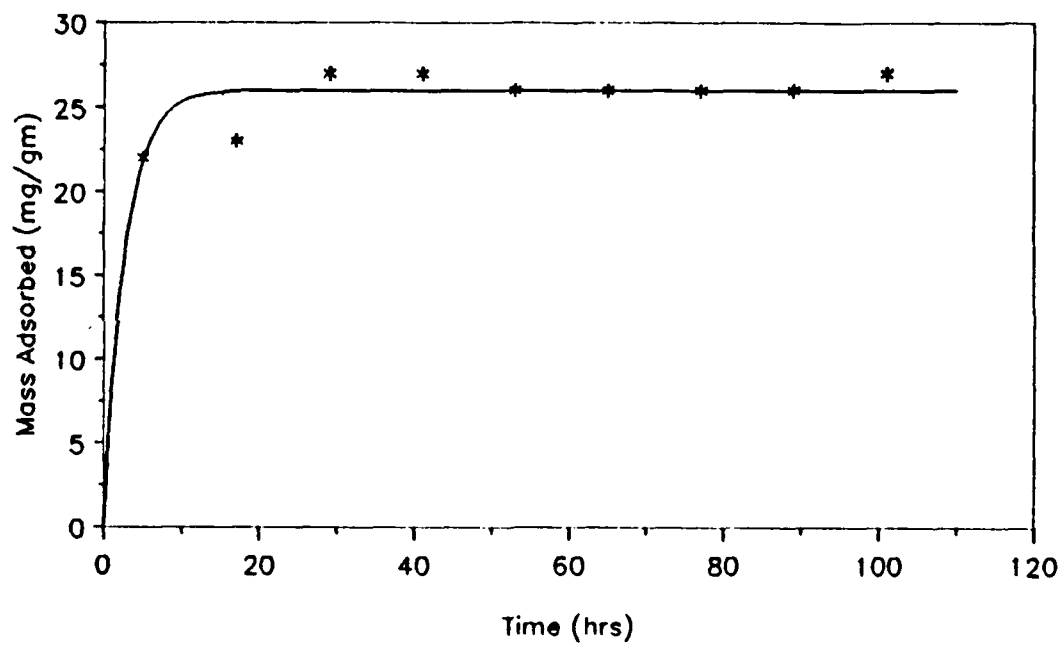


Figure 5.12. Rate of Surfactant Adsorbing to Charleston Soil

Equilibrium Sorption Studies

Naphthalene Adsorption Isotherms

Adsorption isotherms for the Charleston, Greenville and California soils were developed as described in Chapter IV. SAS was used to fit the linear model

$$r = K_d(C_e) \quad (4.19)$$

to the experimental observations obtained. The results of these analyses are given in Figures 5.13, 5.14 and 5.15. Each point plotted represents the average of ten observations, while the bars represent the 95 percent confidence interval estimates. The solid line represents the least squares regression fit of the averaged data points. The high values for R^2 reported in Table 5.6, none less than 0.95, indicate that the model fit the data very well. The data and calculations for these isotherms are given in Appendix D.

The 95 percent interval estimates shown on each figure give an indication of the variability of the data. Very little variability was observed for the Charleston soil. Greater variability was noted for the Greenville soil, and even more for the California soil. This most probably is due to the relative amounts of silt contained in each of the soils along with the method used to prepare the samples. In all cases, approximately one gram of dry soil was weighed into the microvial experimental unit. Prior to taking this "grab sample" the soil was mixed by shaking and rotating the soil container. Particularly for the California soil which had more than 38 percent silt, the silt had a tendency to clump preventing the clay fraction from dispersing homogeneously throughout the soil within the container during the blending process.

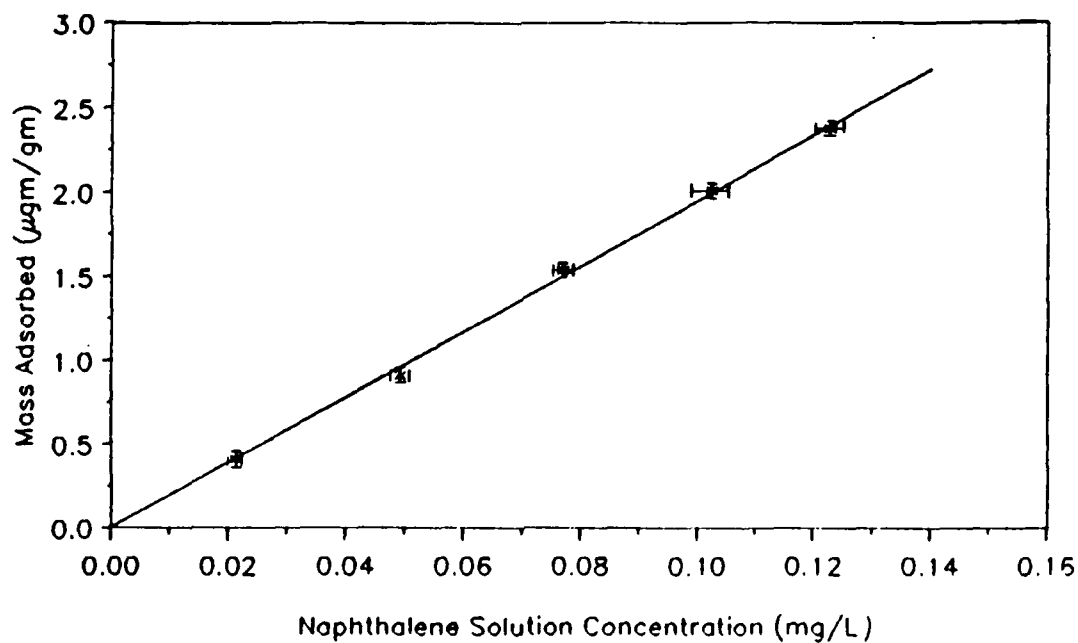


Figure 5.13. Adsorption Isotherm for Naphthalene and Charleston Soil

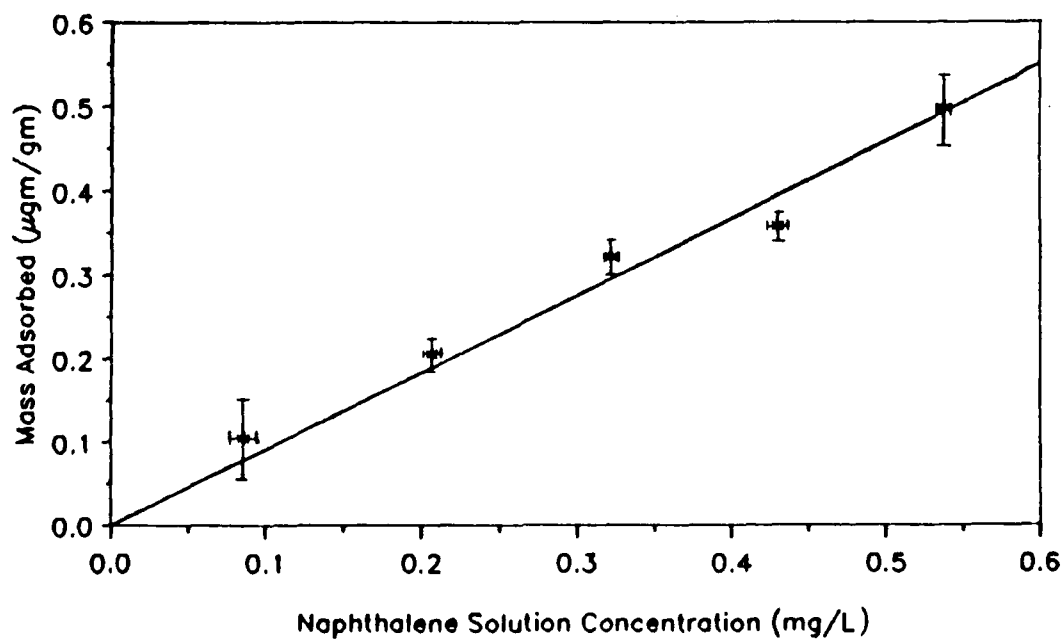


Figure 5.14. Adsorption Isotherm for Naphthalene and Greenville Soil

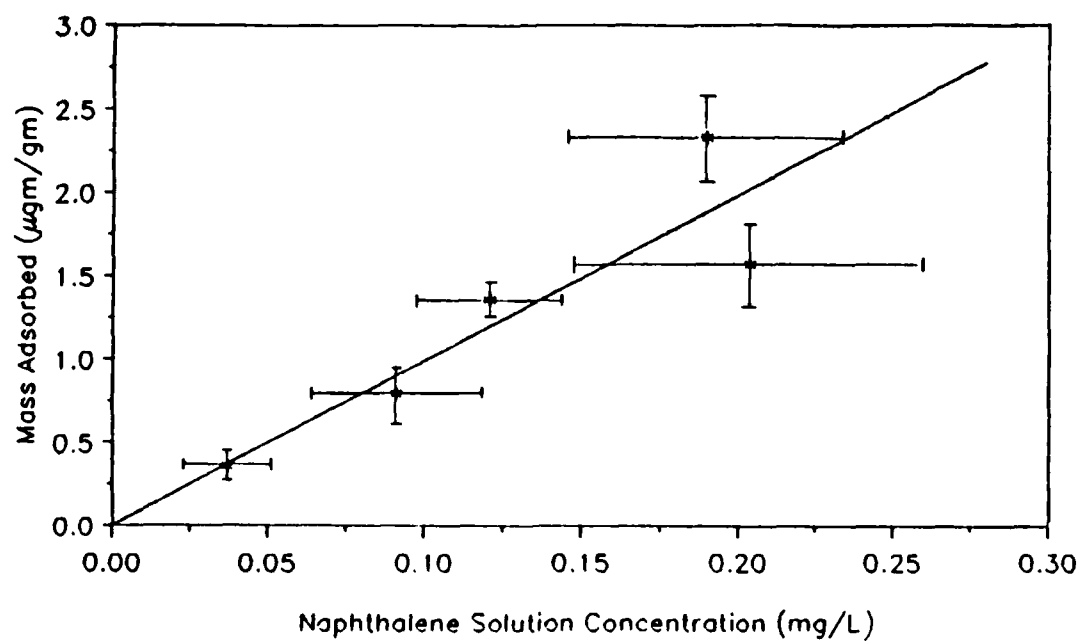


Figure 5.15. Adsorption Isotherm for Naphthalene and California Soil

On this account, the grab samples were not as homogeneous as might be desired. This was also the case for the Greenville soil, but the variability was not as great since it had less silt (19.2 percent). Because the Charleston soil, in contrast, contained nearly two and one-half times more clay than silt, the silt content did not influence soil sample homogeneity.

Table 5.6. Results of Statistical Analysis of Adsorption Data for the Charleston, Greenville and California Soils

Soil	K_d (L/kg)	R^2
Charleston	19.47	0.999
Greenville	0.92	0.995
California	9.79	0.958

The slopes of the regression lines are the values of the partition coefficients (K_d) reported in Table 5.6. The relative values were as expected when considering the results of the naphthalene adsorption kinetic studies. The Charleston soil showed the greatest extent of adsorption as shown by the partition coefficient which had a value equal to 19.47 L/kg. The Greenville soil showed the least extent of sorption with K_d equal to 0.92 L/kg. The extent of sorption exhibited by the California soil fell between the other two and had a K_d equal to 9.79 L/kg.

A search of the literature for reported values of partition coefficients for the adsorption of naphthalene onto soils was made for

comparison purposes. It was recognized that direct comparisons would be difficult based on the fact soils are inherently different. In fact, as previously discussed, there can be substantial variability within one particular soil type used for these type of experiments.

The literature search yielded two applicable publications. Fu and Luthy (1986) developed sorption isotherms for naphthalene and two soils classified as silt loams, and one soil classified as a sand. The reported partition coefficients were 8.0 and 8.5 L/kg for the two silt loams and 2.0 L/kg for the sand. From the particle size distributions calculated for the soils used in this study, the Charleston soil is classified as a fine sandy loam, the California soil as a loam and the Greenville soil as a coarse sandy loam. Although the soils used by Fu and Luthy do not fall into the same categories as those used in this study, the loams would be most similar to the Charleston and California soils, whereas, the sand would be most similar to the Greenville soil. Comparing the partition coefficients for these soils, the Charleston soil has a relatively high K_d , whereas the California and Greenville soils compare favorably with their counterparts from Fu and Luthy's work.

Stauffer and MacIntyre (1986) also reported on the adsorption of naphthalene. These researchers calculated partition coefficients for the adsorption of naphthalene onto four different sorbents; gibbsite, goethite, a surface soil and an aquifer material. The K_d s reported for gibbsite and goethite were 0.15 L/kg and 1.85 L/kg, respectively. For the aquifer material, they determined a K_d of 0.15 L/kg, and for the surface soil a K_d of 8.18 L/kg. Since the Greenville soil contained 50 percent gibbsite and 40 percent kaolinite, its partition coefficient of

0.92 L/kg appears to be consistent in light of the partition coefficient reported for gibbsite. The aquifer material used by Stauffer and MacIntyre was obtained from Lula, Oklahoma. Although an adsorption isotherm was not prepared for the Tinker soil, the kinetic studies showed very little adsorption. Since both the Lula aquifer material and the Tinker soil originated from Oklahoma, it is not surprising that both exhibited similar low extents of adsorption. The K_d for the surface soil used by Stauffer and MacIntyre compared most favorably with the K_d determined for the California soil. Once again, the Charleston soil exhibited larger partition coefficients than any of those reported. It is important to note that, Stauffer and MacIntyre (1986) made no mention of a kinetic study, and they used equilibration times of 24 hours. The results of the kinetic studies conducted as part of this investigation showed that more than two weeks was required to attain 95 percent of the soil's equilibrium sorption capacity in the case of the Charleston soil. Had those researchers provided for longer solute/sorbent contact times, they may have seen greater extents of adsorption.

Before describing the naphthalene desorption studies, the effect that organic carbon may have had on the results of these experiments needs consideration. The importance of soil organic carbon concerning sorption of organic contaminants was presented in Chapter II. The organic carbon content of all the aquifer materials used for this study was less than 0.15 percent, and an attempt was made to determine the extent to which the fraction organic carbon may have influenced the results of these studies. This was accomplished by using the linear model presented in Chapter II relating the octanol-water coefficient, K_{ow} , and the partition coefficient normalized to organic carbon content, K_{oc} .

$$\log K_{oc} = a \log K_{ow} + b \quad (2.13)$$

Since $K_{oc} = K_d/f_{oc}$, where f_{oc} is the fraction organic carbon content of the soil, knowing K_{ow} , f_{oc} and the parameters a and b , an estimate for the partition coefficient, K_d , can be calculated. From Table 4.1, the $\log K_{ow} = 3.37$, and from Table 5.1, the fractions of organic carbon for the Charleston, California and Greenville soils are 0.00062, 0.00141 and 0.00069, respectively. Values for a and b were found in the literature that were determined using a lot of compounds including naphthalene. Lyman *et al.* (1982) reported two sets of applicable values. The first set of values was $a = 0.937$ and $b = 0.006$. Based on these values the estimates of K_d shown below were calculated.

Charleston soil - $K_d = 0.88$ L/kg
 California soil - $K_d = 2.00$ L/kg
 Greenville soil - $K_d = 0.98$ L/kg

The other set of a - b values was $a = 1.00$ and $b = -0.21$. For these values the K_d s shown below were calculated.

Charleston soil - $K_d = 0.90$ L/kg
 California soil - $K_d = 2.04$ L/kg
 Greenville soil - $K_d = 1.00$ L/kg

Both sets of a - b values gave similar approximations for K_d . A comparison of these estimates with the K_d values determined from this study provides an indication of the influence organic carbon may have had in the sorption process. For the Charleston soil, the estimates are significantly below that determined for this study, $K_d = 19.47$ L/kg. Based on this, naphthalene adsorption onto the Charleston soil appears to not be significantly influenced by the presence of organic carbon. Rather, the extent of adsorption predominately is due to the minerals present because more adsorption was observed than could be accounted for considering the fraction organic content of the soil.

For the California soil, the K_d estimates are closer to the value of K_d determined from these studies, $K_d = 9.79$ L/kg. However, the estimates shown above may be high because, as mentioned at the beginning of this chapter, it was suspected that the reported fraction organic content for the California soil was higher than actual due to iron interference in the method of analysis. Although the organic carbon content may have influenced naphthalene sorption to the California soil, once again, it is more likely that the expandable clays were the predominate factor in the sorption process.

For the Greenville soil, the estimates for K_d from K_{oc} shown above are very similar to the value of 0.92 L/kg determined from these studies. This indicates that the organic carbon in the soil may have significantly influenced the sorption of naphthalene with this soil, however, it is also likely that minerals present in the soil influenced the extent of sorption as well.

Naphthalene Desorption Studies Using Surfactants

These experiments were performed as described in Chapter IV. As stated previously, the surfactant used was selected based on its performance when used with the Charleston soil. The same surfactant also was used with the Greenville and Charleston soils to ascertain its effectiveness for mobilizing naphthalene from either of these soils. The results of these experiments are presented by discussing each soil type individually, and then showing how the concentration of surfactant to be used in the column studies was determined. Data and calculations for all soils are presented in Appendix E.

Before discussing the desorption (mobilization) data, however, it is important to emphasize once again that the desorption data was

obtained for experimental units that had first been used to obtain the requisite adsorption isotherm data already reported. After the adsorption isotherm samples had been analyzed, they were diluted approximately 50 percent using a naphthalene-free surfactant solution. That is, if a 1.0 percent surfactant solution was added for the desorption study, the actual surfactant concentration in the vial was approximately 0.5 percent.

Charleston Soil

A desorption isotherm was prepared for each of the five surfactant concentrations used. The isotherms were linear allowing application of the same model used to characterize the adsorption isotherms discussed in the previous section. The data points and least-squares regression lines were plotted along with the adsorption isotherm developed in the previous section to provide a framework for comparison. The results are shown in Figures 5.16 through 5.20, and a summary of the statistical analysis is presented in Table 5.7.

The results of the desorption study conducted when no surfactant was present is shown in Figure 5.16. The partition coefficient, K_d' , or slope of the regression line, appears to have increased slightly as compared with the adsorption K_d . If this difference could be shown to be statistically significant, the increase in K_d would be an indication of irreversible sorption under the conditions the experiment was conducted.

To evaluate whether a statistically significant difference existed, the Principle of Conditional Error (PCE), as described by Wilczak (1988), was applied by pooling the adsorption and desorption data. The following two-parameter ($p=2$) model was developed:

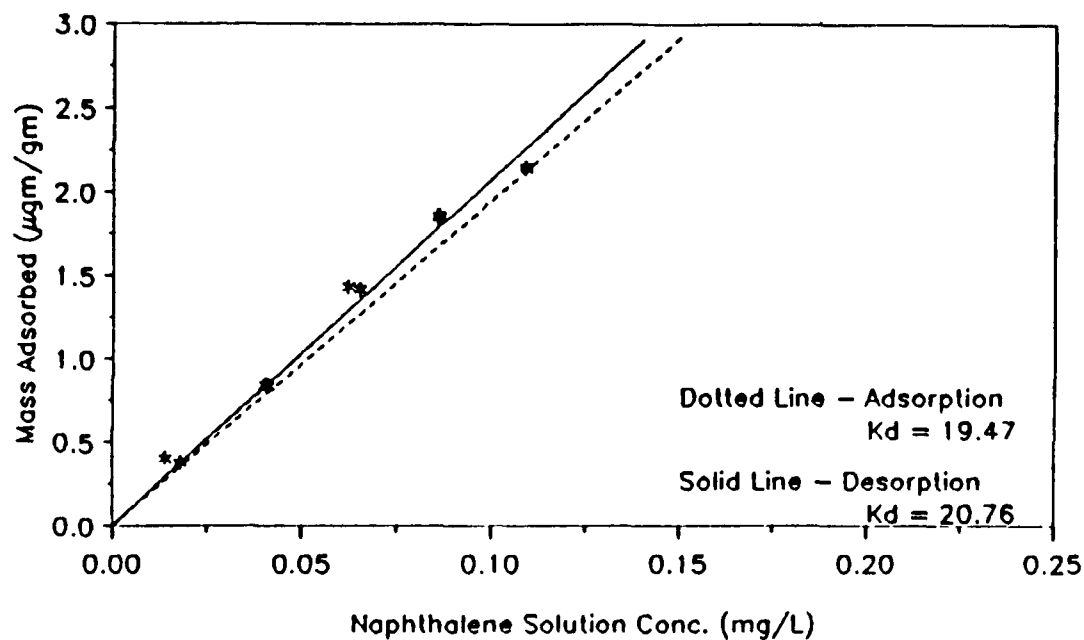


Figure 5.16. Naphthalene Desorption Isotherm for Charleston Soil in the Presence of No Surfactant

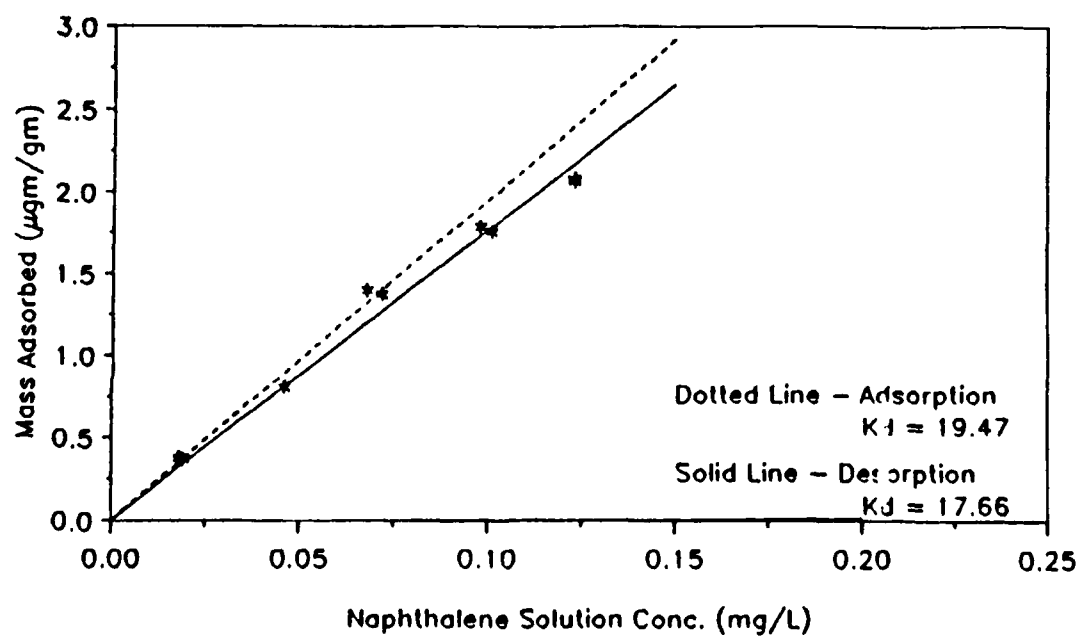


Figure 5.17. Naphthalene Desorption Isotherm for Charleston Soil, 0.01 Percent Surfactant Solution Added

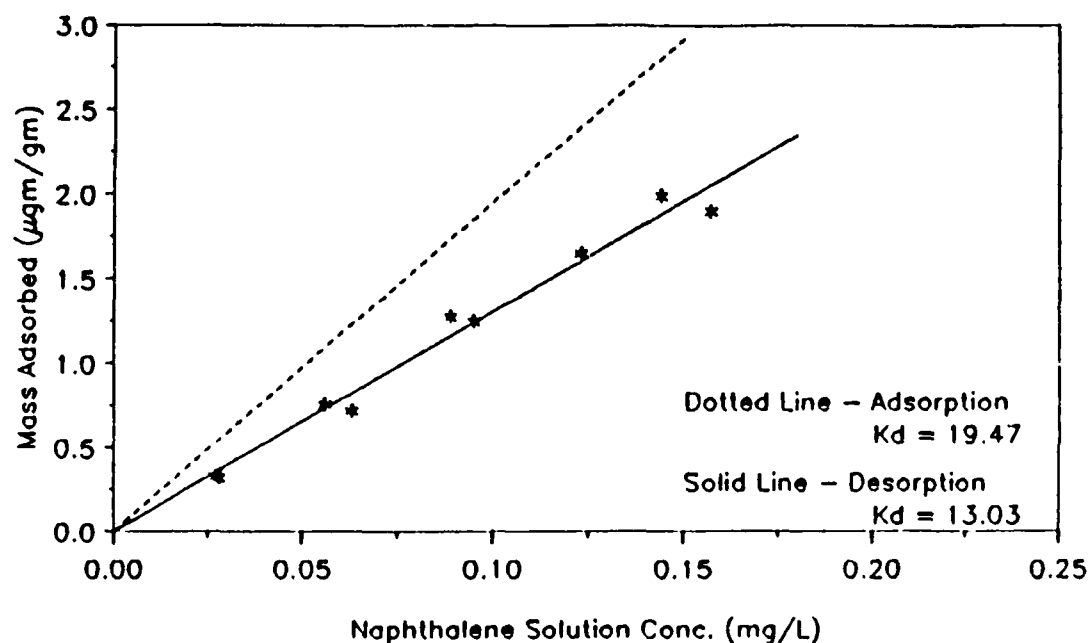


Figure 5.18. Naphthalene Desorption Isotherm for Charleston Soil, 0.05 Percent Surfactant Solution Added

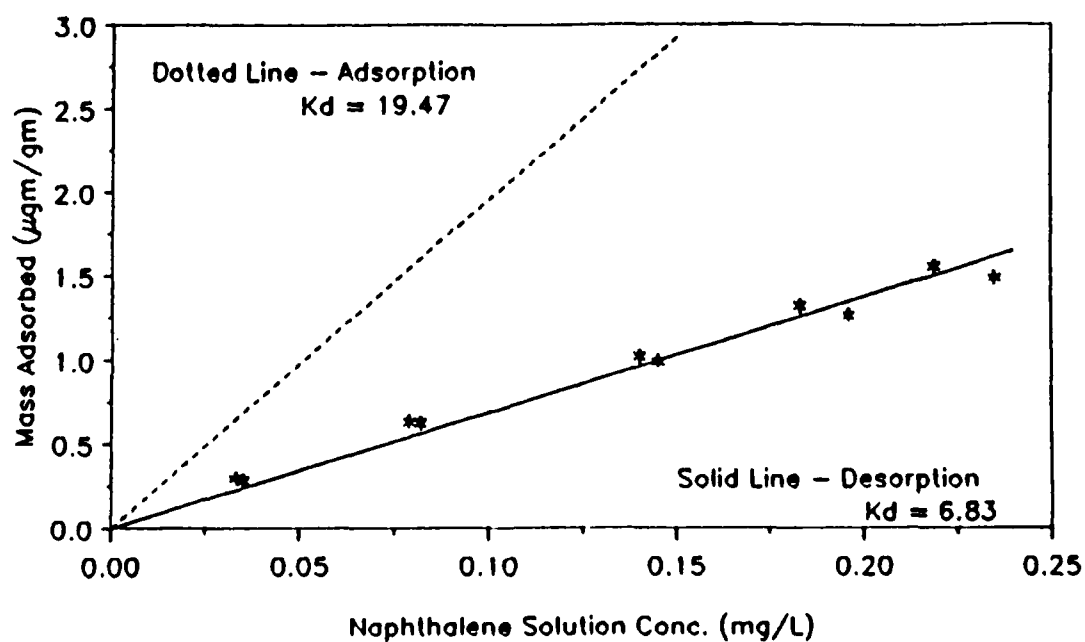


Figure 5.19. Naphthalene Desorption Isotherm for Charleston Soil, 0.25 Percent Surfactant Solution Added

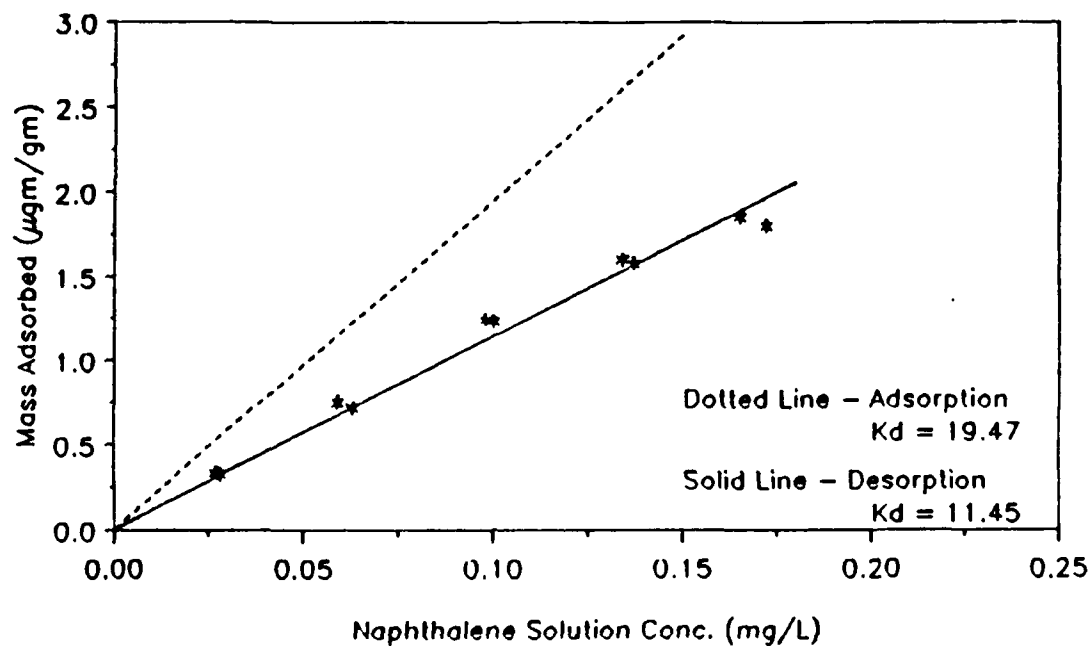


Figure 5.20. Naphthalene Desorption Isotherm for Charleston Soil, 1.00 Percent Surfactant Solution Added

Table 5.7. Summary of Statistical Analysis of Charleston Desorption Data

Percent Surfactant Added	Parameter Estimate and Statistics for Plot of Desorption Isotherm			Statistics for Testing the Hypothesis that the Addition of Surfactants has an Effect on the Desorption of Naphthalene				
	k_d (L/kg)	Standard Error	R^2	Unconditioned Model SSE/df	Conditioned Model SSE/df	Hypothesis SSE/df	Calculated f-statistic	Tabulated F-value
0.00	20.76	0.18	0.999	0.07841/13	0.11184/14	0.03999/1	$f_{1,13} = 6.63$	$F_{1,13,.05} = 4.67$
0.01	17.66	0.39	0.996	0.08262/12	0.15603/13	0.07342/1	$f_{1,12} = 10.66$	$F_{1,12,.05} = 4.75$
0.05	13.05	0.31	0.996	0.06992/12	1.09075/13	1.02083/1	$f_{1,12} = 175.20$	$F_{1,12,.05} = 4.75$
0.25	6.63	0.16	0.995	0.05616/13	4.84654/14	4.79038/1	$f_{1,13} = 1108.88$	$F_{1,13,.05} = 4.67$
1.00	11.45	0.24	0.996	0.06772/13	1.79911/14	1.73139/1	$f_{1,13} = 332.37$	$F_{1,13,.05} = 4.67$

$$\Gamma = Z(K_d)C_e + (1-Z)(K_d')C_e \quad (5.3)$$

where

Γ = mass naphthalene adsorbed per gram soil ($\mu\text{g/g}$),

C_e = equilibrium solution concentration of naphthalene (mg/L),

$Z = 1$ if the observation (Γ, C_e) is from the adsorption experiment,

$Z = 0$ if the observation (Γ, C_e) is from the desorption experiment,

K_d = the parameter representing the partition coefficient for the adsorption experiment,

K_d' = the parameter representing the partition coefficient for the desorption experiment.

When the pooled data are used with this model, least squares estimates for K_d and K_d' are determined along with the residual sum of squares error (SSE) based on the degrees of freedom equal to the number of observations (n_o) minus the number of parameters ($p=2$). This model is then "conditioned" by the hypothesis that $K_d = K_d' = K$, which implies one parametric restriction (rank $r=1$) and results in the single parameter model

$$\Gamma = KC_e. \quad (5.4)$$

The statistical approach provides the least square estimate for K , and the conditioned SSE (or, CSSE) based on degrees of freedom equal to $(n_o - p + r)$. According to the Principle of Conditional Error, the sum of squares of the hypothesis (SSH that $K_d = K_d'$) is equal to the CSSE minus the SSE, with the degrees of freedom equal to the rank of the hypothesis (which in this case equals one). The f -statistic then is calculated by

$$f_{r, (n-p)} = \frac{\text{SSH}/r}{\text{SSE}/(n_o-p)}. \quad (5.5)$$

The hypothesis is rejected when the calculated f -statistic exceeds the critical value taken from the F -distribution with specified Type 1 error rate.

The results of this statistical analysis for the condition in which no surfactant was added are given on the first line of Table 5.7. Applying the PCE shows that the calculated f -statistic exceeds the tabulated F -value and the hypothesis that $K_d = K_d'$ must be rejected leading to the conclusion that a slight extent of irreversible sorption was evident. This concurs with observations made during the sorption kinetic studies. Similar findings also were reported by Katz and Uchrin (1986) for desorption studies developed for aquifer sands and organic contaminants indicating pronounced hysteresis and sorption irreversibility. This finding is significant in that a certain fraction of the naphthalene associated with the soil might be extremely difficult to remove. Undoubtedly, this would decrease the efficiency of the pump and treat remediation process. In addition, it would affect the validity of using the advective/dispersive groundwater transport equation described in Chapter II to model the movement of naphthalene in this soil because reversible sorption was assumed to develop the equation. The effect of this slight amount of irreversibility observed should not be a significant factor. However, it must be recognized that the extent of irreversibility can be influenced by the dilution ratio used for these experiments (approximately 50:50). It is possible that for greater dilutions, i.e., greater amounts of supernatant solution removed and replaced with naphthalene-free solution, the extent of irreversibility can be much greater.

The Principle of Conditional Error was also applied individually to the four sets of observations with varying surfactant concentrations to test the hypothesis that the partition coefficient with surfactant added is the same as the partition coefficient for the adsorption isotherm.

The results listed in Table 5.7 indicate that, in all cases the calculated f -statistic exceeded the tabulated F -value leading to the conclusion that the surfactant did influence desorption at all surfactant concentrations.

When the concentration of the surfactant added was 0.01 percent, a decrease in K_d to 17.66 L/kg was observed as shown in Figure 5.17. Even though the solution concentration, approximately 0.005 percent, is below the CMC (0.024 percent) the surfactant had solubilized some naphthalene. This result is not unexpected since the CMC is a mean value representing the range over which micelle formation occurs. Clearly, micelles are formed at concentrations below the calculated CMC. The isotherm shown in Figure 5.18 indicates that the partition coefficient is further decreased to 13.03 L/kg as the surfactant concentration added is increased to 0.05 percent. This concentration of surfactant added results in a solution concentration of approximately 0.025 percent which is very close to the CMC.

A further increase in the concentration of surfactant added to the vial to 0.25 percent results in an even lower K_d of 6.83 L/kg. A surfactant concentration of approximately 0.125 percent, consequently, reduced the partition coefficient from 19.47 L/kg to 6.83 L/kg; a 65 percent decrease as shown in Figure 5.19.

A further increase in the surfactant concentration added to 1.00 percent results in a value of K_d less than the K_d value for the adsorption isotherm, but greater than the value of K_d resulting from the addition of the 0.25 percent surfactant solution. Gaynor and Volk (1976) reported similar findings in that a 1.0 percent surfactant concentration showed reduced adsorption of picloram on a soil, whereas a 10.0 percent

concentration showed an increase in picloram adsorption. A personal discussion with a representative of a surfactant manufacturer (Clapp, 1989) identified a possible explanation: that is, the characteristics of the surfactant mixture sorbing to a soil may change at higher surfactant concentrations. For the Tween-20/AY-65 mixture, sorption at low concentrations may be due primarily to adsorption of the nonionic surfactant. At higher concentrations, however, hemimicelles may be formed by the anionic surfactant on soil surfaces, providing an organic environment on the soil into which the naphthalene can partition. The CMC for AY-65 alone was calculated to be 3.13 percent. Because hemimicelles would form at lower concentrations, it is likely that when the 1.00 percent surfactant solution was added to the system, the AY-65 formed hemimicelles resulting in a reduction in the efficiency of the surfactant blend.

To test whether there is indeed a minimum K_d (i.e., a most efficient surfactant concentration), the Principle of Conditional Error was applied by pooling the data obtained from the experiments using the 0.05 and 0.25 percent surfactant levels, with the hypothesis that both partition coefficients were the same. This was performed once again by pooling the data obtained from the experiments where 0.25 and 1.00 percent surfactant concentrations were used. The results of these statistical tests are shown in Table 5.8. In both cases the hypothesis that the partition coefficients are equal was rejected leading one to conclude that there exists a minimum K_d . It cannot be said that the 0.25 percent concentration of surfactant gave the minimum K_d , only that there is a concentration that produces a minimum, and that that concentration lies somewhere between 0.05 and 1.00 percent added, which is a solution

concentration of surfactant that lies between 0.025 and 0.50 percent. This phenomenon will be discussed further after the results obtained for the Greenville and California soils are presented.

Table 5.8. Summary of Testing Hypothesis that Partition Coefficients are Equal for 0.05, 0.25 and 1.00 Percent Surfactant Solutions Added

Hypothesis	Unconditioned Model SSE/df	Conditioned Model CSSE/df	SSH/df	Calculated f-Statistic	Tabulated F-Value
$K_d(.05) =$ $K_d(.25)$	0.11711/ 17	2.53173/ 18	2.41462/ 1	$f_{1,17}=350.51$	$F_{1,17,.05}=4.45$
$K_d(1.0) =$ $K_d(.25)$	0.11491/ 18	1.81824/ 19	1.70333/ 1	$f_{1,18}=266.82$	$F_{1,18,.05}=4.41$

Although detailed desorption studies using surfactants have not been found in the literature to enable comparison with the results of these experiments, four reports were identified to give insight as to the generality of these results.

Scholz et al. (1983) investigated the use of a nonionic surfactant, Tween 80, to aid in the removal of PCBs from a surface soil. They reported 37.5 percent removals of PCBs with a 1.0 percent surfactant solution, whereas, water alone showed a 24.6 percent removal. In this instance, the surfactant solution increased the efficiency of PCB removal by approximately 52 percent. Even though the compounds and soils used were different than those used in this study, the results are similar to those for naphthalene and the Charleston soil.

Column studies conducted by Rickabaugh et al. (1987) showed that less than one percent of the organic contaminants that were adsorbed to

a surface soil were removed by using water alone, whereas a nonionic/cationic surfactant blend at a solution concentration of 2.0 percent removed approximately 59 percent. This increase in removal efficiency over water alone is much greater than the increase shown in this study.

MTA Remedial Resources Inc. (MTARRI, undated) developed a commercial process using surfactants to aid in the remediation of contaminated aquifers. They claim a 50 to 80 percent reduction in the costs associated with the remediation when compared with the commonly used pump and treat procedure. In Chapter II, a hypothetical situation was used to illustrate that a decrease in the partition coefficient of approximately 50 percent increased the mobility of the contaminant by approximately the same amount. If one accepts the premise that this increase in mobility is directly related to the efficiency in contaminant removal, which, in turn is directly related to the cost of contaminant removal, then a 50 to 80 percent reduction in costs reported by MTARRI compares favorably with the results of the present investigation.

Fu and Luthy (1986) reported results that were somewhat analogous to those described in this study. However, instead of using surfactant solutions, they used polar organic solvents, methanol and acetone, to mobilize naphthalene. Linear sorption isotherms were developed with the solvents ranging in concentration from zero to 50 percent by volume. The resulting naphthalene sorption isotherms were linear, similar to the isotherms developed in this study, and showed that the slope of the isotherm, i.e., the partition coefficient, decreased as the volume percent of solvent increased. Using a silt loam as the model sorbent, the partition coefficient decreased from 8.0 L/kg at zero percent methanol to 0.7 L/kg for a 50 percent methanol solution. The results for acetone

were similar. A 20 percent solution of methanol resulted in a reduction in K_d of approximately 50 percent, which is approximately equivalent to the solubilization level obtained in this study when a 0.125 percent surfactant solution was used.

Greenville Soil

The desorption studies using the Greenville soil were performed in the same manner as those for the Charleston Soil. The resulting desorption isotherms for water alone and the four different surfactant concentrations are shown in Figures 5.21 through 5.25. A summary of the corresponding statistical analyses performed is presented in Table 5.9.

An increase in the slope of the isotherm for the desorption of naphthalene in the presence of water alone is illustrated in Figure 5.21. The adsorption partition coefficient was 0.92 L/kg while the desorption coefficient was determined to be 1.02 L/kg. Again, if the difference was found to be statistically significant, one could conclude that some of the sorption was irreversible. However, using the PCE to test whether both partition coefficients were equal, the f -statistic was calculated to be less than the tabulated F -value as shown in Table 5.9, resulting in a failure to reject the hypothesis that both partition coefficients were the same. In this case, the data was more scattered than for the Charleston soil, and this variability affected the ability to detect any evidence of irreversibility. However, because the types of minerals present did not include expandable clays, irreversible sorption was not particularly expected.

The extent of naphthalene solubilization (desorption) for increasing surfactant concentrations is illustrated in Figures 5.22 through

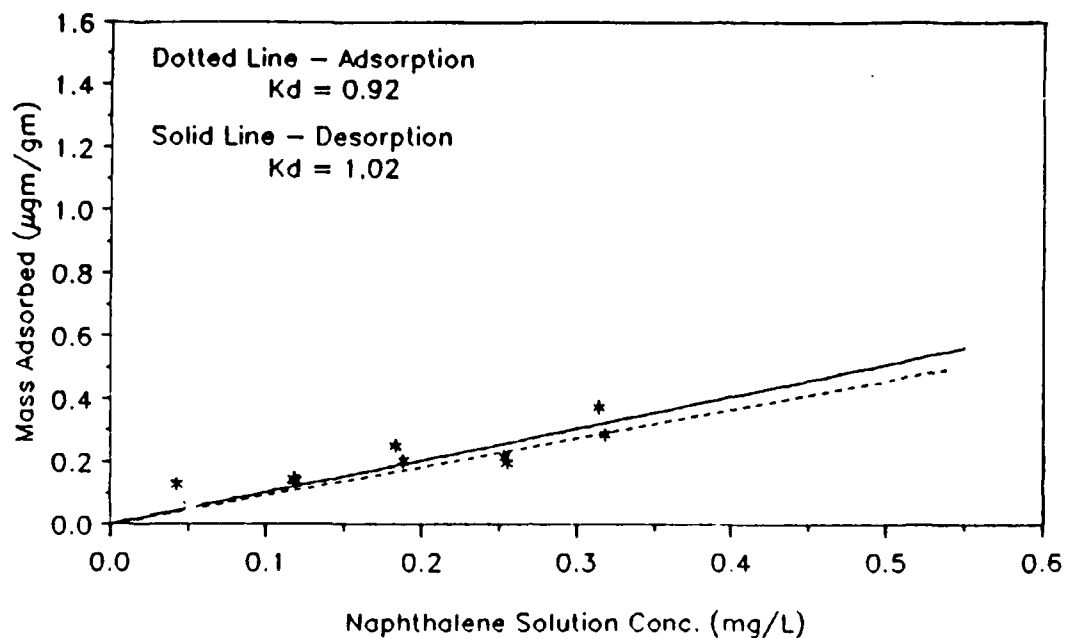


Figure 5.21. Naphthalene Desorption Isotherm for Greenville Soil in the Presence of No Surfactant

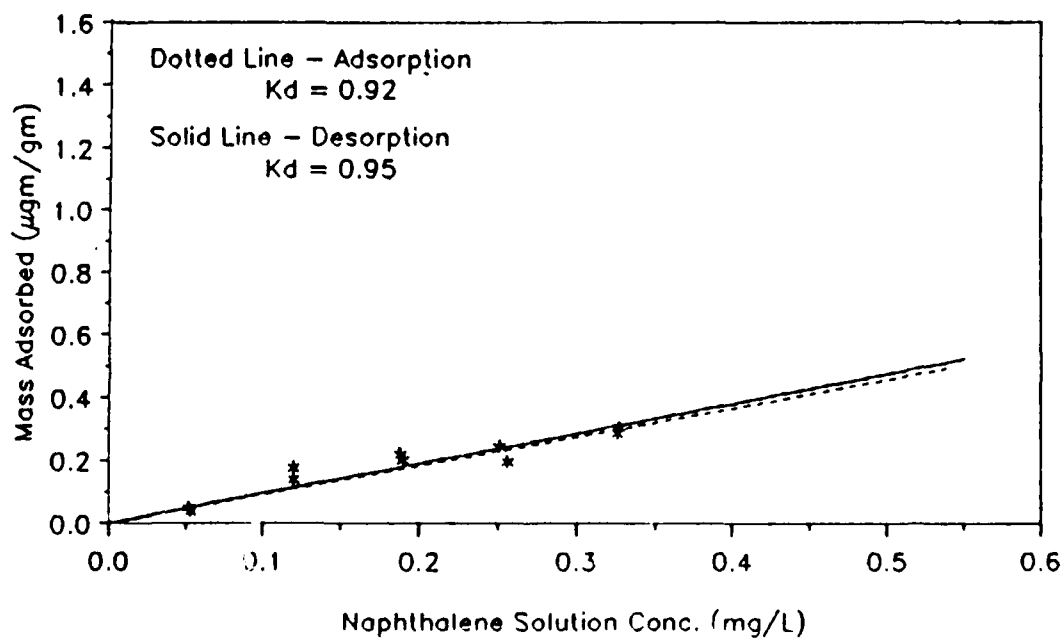


Figure 5.22. Naphthalene Desorption Isotherm for Greenville Soil, 0.01 Percent Surfactant Solution Added

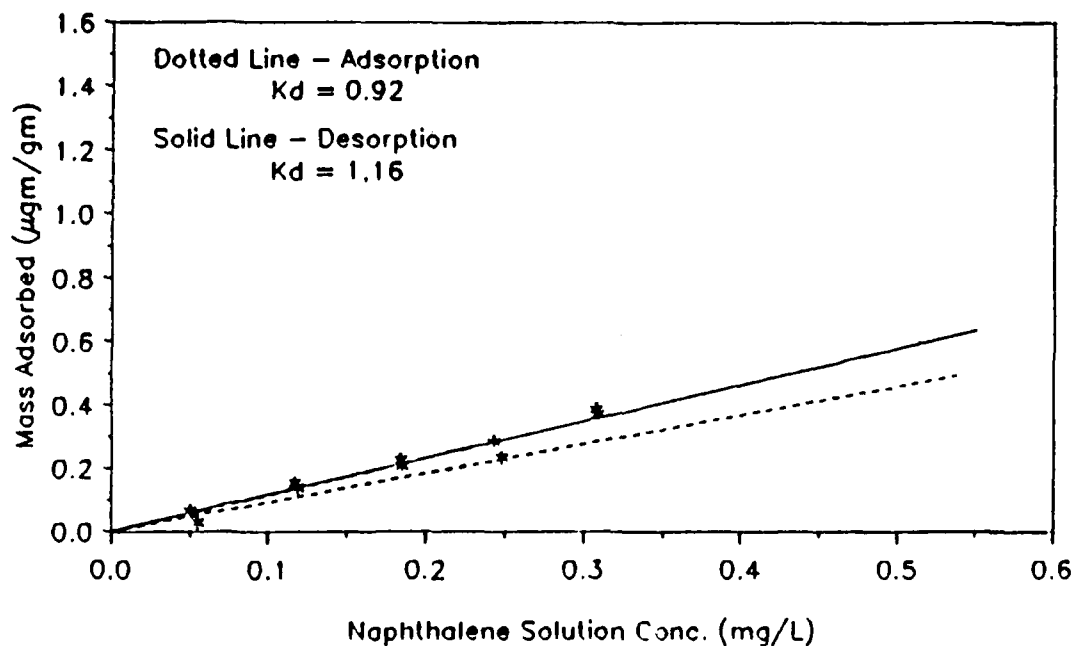


Figure 5.23. Naphthalene Desorption Isotherm for Greenville Soil, 0.05 Percent Surfactant Solution Added

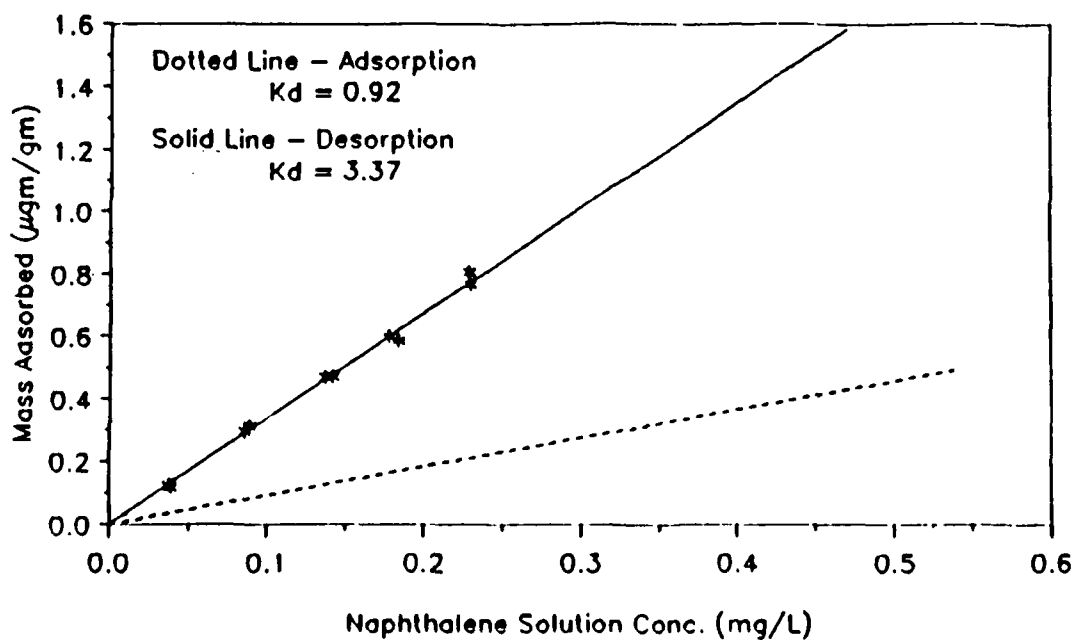


Figure 5.24. Naphthalene Desorption Isotherm for Greenville Soil, 0.25 Percent Surfactant Solution Added

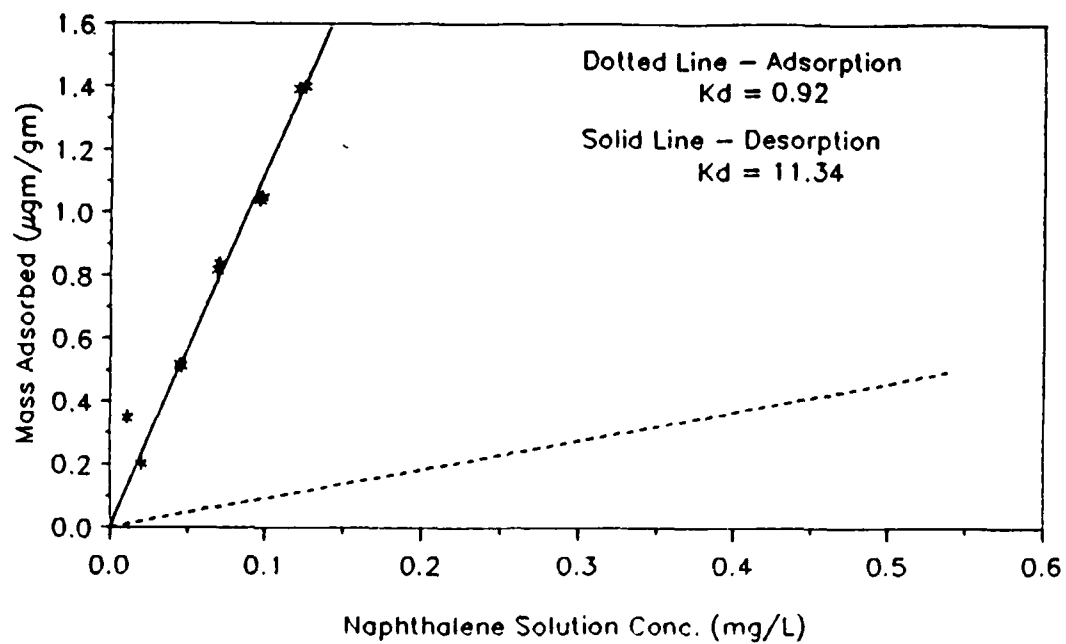


Figure 5.25. Naphthalene Desorption Isotherm for Greenville Soil, 1.00 Percent Surfactant Solution Added

Table 5.9. Summary of Statistical Analysis of Greenville Desorption Data

Percent Surfactant Added	Parameter Estimate and Statistics for Plot of Desorption Isotherm			Statistics for Testing the Hypothesis that the Addition of Surfactants has an Effect on the Desorption of Naphthalene				
	K_d (L/kg)	Standard Error	R^2	Unconditioned Model SSE/df	Conditioned Model SSE/df	Hypothesis SSE/df	Calculated f-statistic	Tabulated F-value
0.00	1.02	0.08	0.953	0.02503/13	0.02778/14	0.00275/1	$f_{1,13} = 1.43$	$F_{1,13,.05} = 4.67$
0.01	0.35	0.05	0.977	0.01247/13	0.01283/14	0.00036/1	$f_{1,13} = 0.37$	$F_{1,13,.05} = 4.67$
0.05	1.16	0.04	0.990	0.00874/13	0.02302/14	0.01428/1	$f_{1,13} = 21.24$	$F_{1,13,.05} = 4.67$
0.25	3.37	0.04	0.999	0.00590/13	1.01688/14	1.01097/1	$f_{1,13} = 2226.14$	$F_{1,13,.05} = 4.67$
1.00	11.34	0.32	0.993	0.06210/13	6.26009/14	6.19799/1	$f_{1,13} = 1237.49$	$F_{1,13,.05} = 4.67$

5.25. What is clear is that the results are strikingly different than those obtained for the Charleston soil. In fact, no solubilization was observed. Rather, the partition coefficients increased as the surfactant concentration increased.

For the 0.01 percent surfactant solution, the adsorption and desorption regression lines are nearly coincidental. The statistical analysis summarized in Table 5.9 indicates that there was not evidence of a difference in partition coefficients for the adsorption isotherm and the desorption isotherm. The conclusion is that the surfactant at this concentration level had no effect on the solubilization of naphthalene.

As the surfactant concentrations were increased above 0.01 percent, the partition coefficients increased as well, each showing a statistically significant effect. The K_d for the experimental system in which the 0.05 percent surfactant solution was used increased to 1.16 L/kg. The K_d increased even further to 3.37 and 11.34 L/kg for the experimental systems in which 0.25 and 1.00 percent surfactant solutions were applied, respectively. The latter experimental system showed nearly a 12 fold increase over the value of K_d obtained for water alone. These results were contrary to what was anticipated, and an additional test was conducted in an effort to explain the observations.

It was theorized that this phenomenon occurred due to surfactant sorption. Single point isotherm studies accomplished during the preliminary phase of this study showed that 53.2 percent of the surfactant adsorbed to the Greenville soil, whereas only 40.3 percent adsorbed to the Charleston soil. The fact that more surfactant adsorbed to the Greenville soil appeared significant, particularly when considering

that greater extent of adsorption would be expected for the Charleston soil due to its much greater amounts of surface area available.

A review of the literature concerning zero points of charge (Schulthess and Sparks, 1986; Bohn *et al.*, 1985) showed that the types of minerals making up the clay fraction of the Greenville soil, gibbsite and kaolinite, had surface charges that were highly pH dependent. Preliminary studies conducted to determine the zero points of charge for the Charleston and Tinker soils were unsuccessful because these soils consisted of minerals, primarily expandable clays, that have so much structural charge that any pH dependent charge was overwhelmed. Although a determination of the ZPC was not attempted for the California soil, its clay mineralogy is similar to the Charleston soil and would most likely also show a highly negatively charged surface. The ZPC determination also was not attempted for the Greenville soil during the preliminary studies. It was erroneously assumed at that time that any results obtained would be the similar to those obtained for the Charleston and Tinker soils.

In an attempt to explain the solubilization data obtained for the Greenville soil, the zero point of charge was determined for this soil. The experiment was conducted according to the procedure described by Schulthess and Sparks (1986) and statistically analyzed using a method described by Wilczak (1988). The experimental method consists of an acid/base titration of the soil solution at three different ionic strengths. The intersection of the three titration curves is defined as the zero point of charge. The titration curves are modeled as ogives, and the method of Wilczak (1988) produces the least squares estimate for the zero point of charge along with its 95 percent interval estimate.

The results of the experiment are shown in Figure 5.26, and the zero point of charge was determined to be $\text{pH} = 5.38 \pm 0.68$.

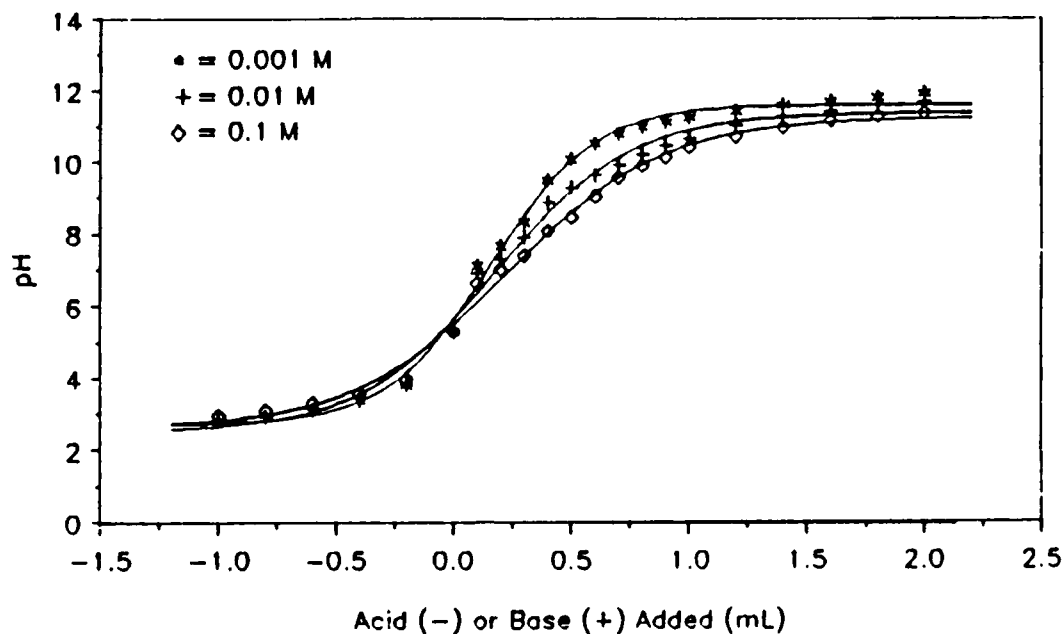


Figure 5.26. Greenville Soil Titration Curves at Three Concentrations of Calcium Chloride

The solution pH of the samples used in the desorption experiments was monitored as explained in Chapter IV. For the Greenville soil, the pH ranged from 4.90 when a 0.01 percent surfactant solution was added to the vials to 5.36 when a 1.00 percent solution was added. At the pH_{zpc} , the number of positively charged adsorption sites equals the number of negatively charged adsorption sites. For the Charleston soil, the surface was determined to be predominately negative, with relatively few, if any, positive sites. In contrast, because the zero point of charge of the Greenville soil was determined to be very close to the pH of the

solutions used in the sorption studies, approximately half of the charged sites were positive which permitted much greater adsorption of anionic surfactant due to electrostatic attraction.

As described for the Charleston soil, it was postulated that the partition coefficients began to increase when the anionic surfactant began forming hemimicelles. Hemimicelle formation occurs when the soil surface coverage by the anionic molecule increases to the extent where the hydrophobic chain can no longer lie flat against the surface. In this case, the molecules orient themselves in a position where the hydrophobic portions of the molecules are pointed away from the surface while the anionic hydrophiles are specifically adsorbed to the positive sorption site. The hydrophobic portion of surfactant molecules in solution then associate with the hydrophobic portion of the adsorbed molecule forming a double layer of surfactant molecules. This produces a hydrocarbon-like phase between the layers, into which the naphthalene can partition. Since a hemimicelle is affixed to the soil surface, any naphthalene that partitions into the hemimicelle is removed from solution.

For the Greenville soil, then, the anionic surfactant is strongly adsorbed because of the large numbers of positively charged adsorption sites, and surfactant surface coverage is attained rapidly because of the relatively small amount of surface area. This results in the formation of hemimicelles at relatively low surfactant concentrations. The first evidence of hemimicelle formation occurred with the 0.05 percent surfactant solution where there was evidence of increased naphthalene adsorption. As surfactant concentrations were further increased, hemimicelle formation increased resulting in an apparent increase in naphthalene adsorption.

These results demonstrate a very significant point. The purpose of using a surfactant solution is to increase the solubilization of naphthalene or any target contaminant. While the surfactant effectively performed that function for the Charleston soil, the opposite effect was observed for the Greenville soil. The types of clays and minerals present have a profound effect on the efficiency of the surfactant solution.

The results of the Greenville soil desorption study are not unique. Gaynor and Volk (1976) investigated the use of surfactants to mobilize herbicides from soils. They reported that for the soils used in their investigations, depending on the soil type, nonionic surfactants would either increase or decrease contaminant adsorption, cationic surfactants always increased adsorption, and higher concentrations of anionic surfactants increased adsorption.

California Soil

The isotherms resulting from the five desorption experiments conducted with the California soil are shown in Figures 5.27 through 5.31. A summary of the statistical analyses of the results is presented in Table 5.10. It appeared that at very low surfactant concentrations the scatter of the data was more pronounced than at higher concentrations. This is indicated by the lower coefficients of correlation, 0.843 and 0.796, for the experiments conducted with no surfactant and 0.01 percent surfactant added, respectively. As surfactant concentration increased, the scatter diminished, and the coefficients of correlation improved. This may be attributed to the fact that naphthalene has a higher affinity for the hydrocarbon core of micelles than for the surfaces of the

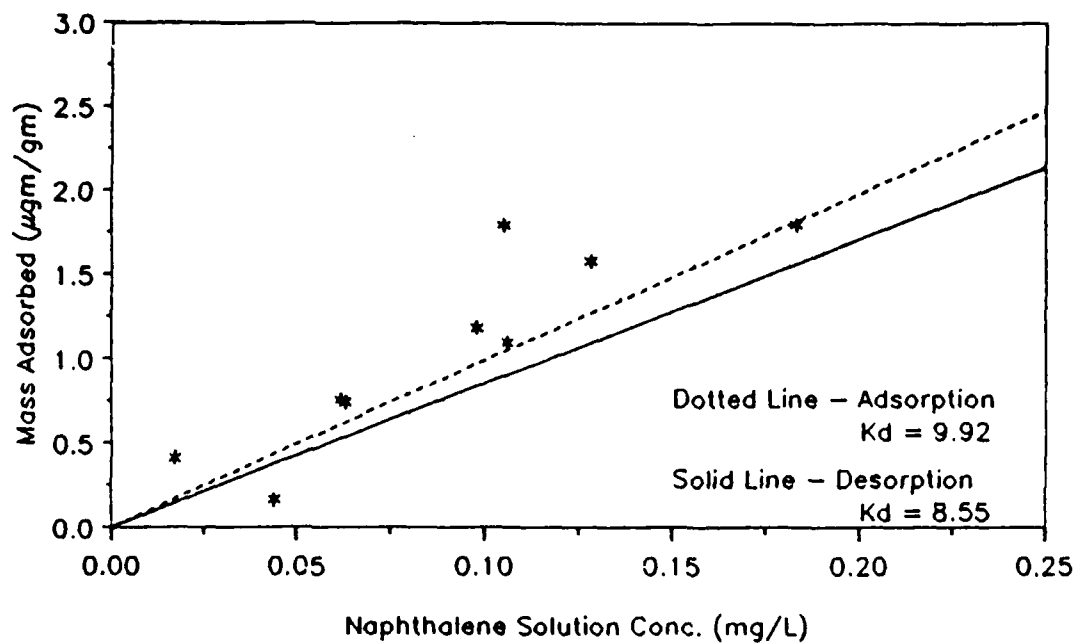


Figure 5.27. Naphthalene Desorption Isotherm for California Soil in the Presence of No Surfactant

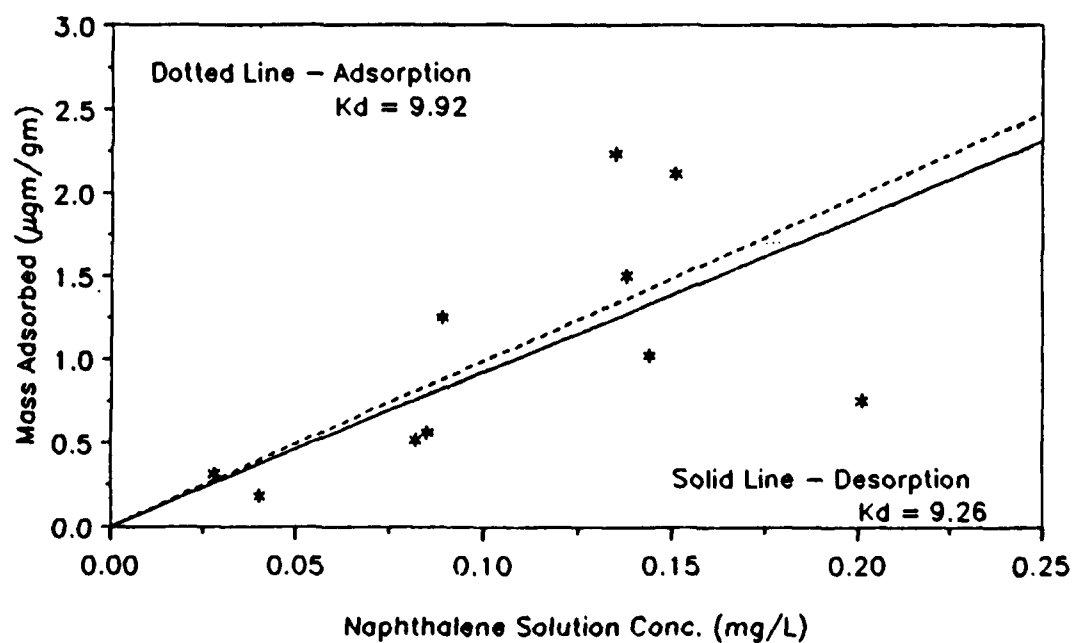


Figure 5.28. Naphthalene Desorption Isotherm for California Soil, 0.01 Percent Surfactant Solution Added

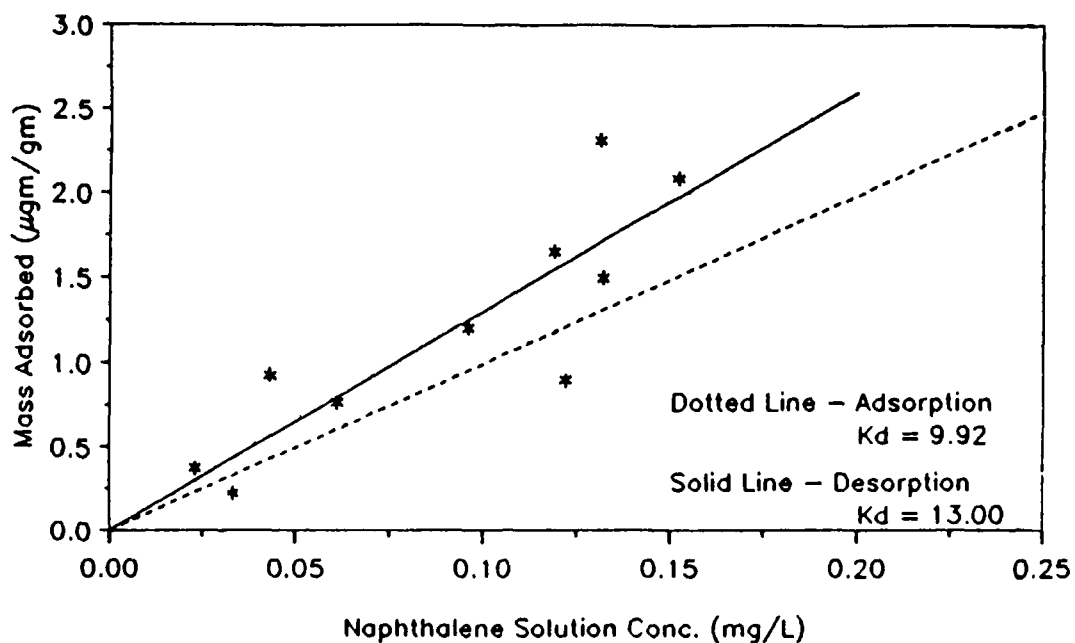


Figure 5.29. Naphthalene Desorption Isotherm for California Soil, 0.05 Percent Surfactant Solution Added

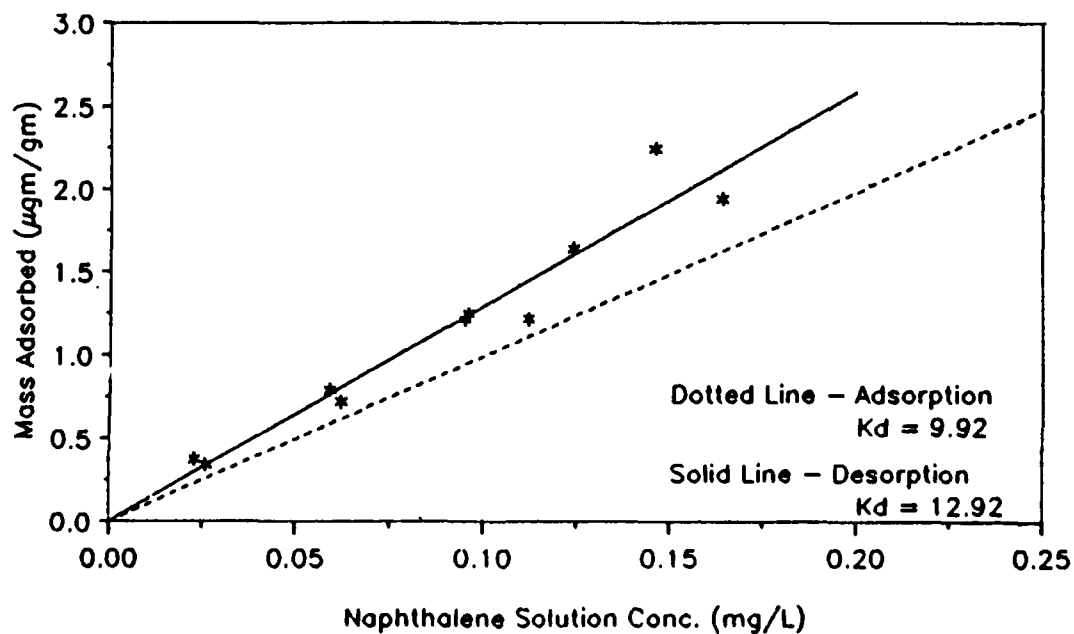


Figure 5.30. Naphthalene Desorption Isotherm for California Soil, 0.25 Percent Surfactant Solution Added

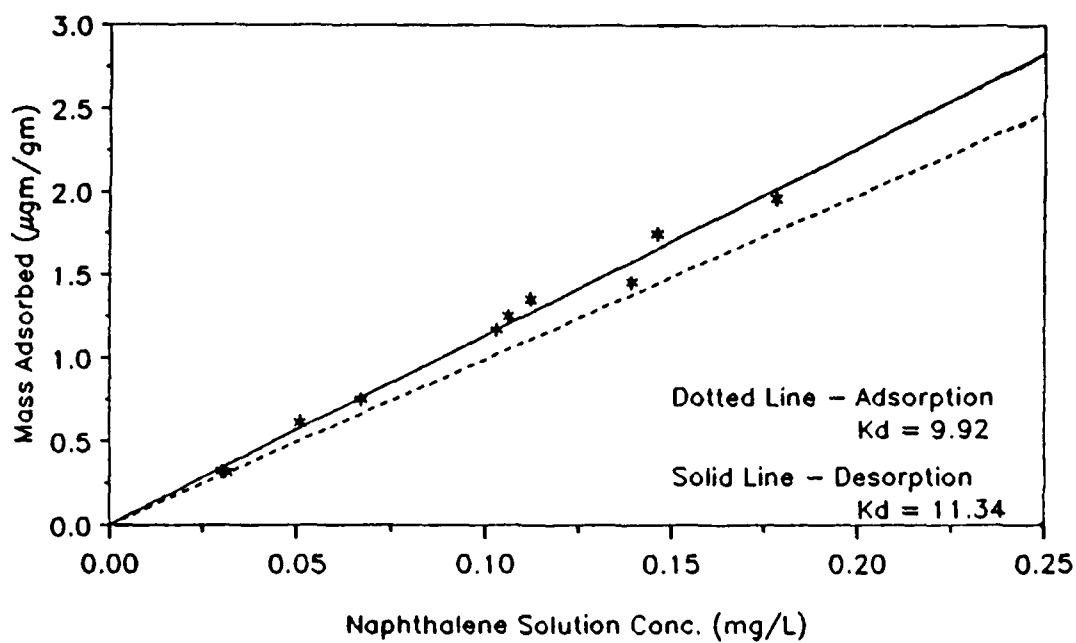


Figure 5.31. Naphthalene Desorption Isotherm for California Soil, 1.00 Percent Surfactant Solution Added

Table 5.10 Summary of Statistical Analysis of California Desorption Data

Parameter Estimate and Statistics for Plot of Desorption Isotherm			Statistics for Testing the Hypothesis that the Addition of Surfactants has an Effect on the Desorption of Napthalene					
Percent Surfactant Added	K_d (L/kg)	Standard Error	R^2	Unconditioned Model SSE/df	Conditioned Model SSE/df	Hypothesis SSE/df	Calculated t-statistic	Tabulated F-value
0.00	6.55	1.27	0.834	2.87279/13	2.99029/14	0.11750/1	$f_{1,13} = 0.53$	$F_{1,13,.05} = 4.67$
0.01	9.26	1.56	0.796	3.63202/13	3.65817/14	0.02150/1	$f_{1,13} = 0.09$	$F_{1,13,.05} = 4.67$
0.05	13.00	1.09	0.941	1.54055/13	2.02799/14	0.48744/1	$f_{1,13} = 4.11$	$F_{1,13,.05} = 4.67$
0.25	12.92	0.50	0.986	0.67143/13	1.13466/14	0.46324/1	$f_{1,13} = 6.97$	$F_{1,13,.05} = 4.67$
1.00	11.34	0.19	0.997	0.47971/13	0.58997/14	0.11026/1	$f_{1,13} = 2.99$	$F_{1,13,.05} = 4.67$

soil. The solution concentration of naphthalene is influenced to a greater extent by the number of micelles present in solution than by adsorption onto the soil. Therefore, as surfactant concentration increases, the amount of solubilized naphthalene increases, and the variability associated with the soil becomes less of a factor regarding the partitioning between sorbent and solution phases.

The naphthalene desorption isotherm in the presence of no surfactant is shown in Figure 5.27. It appears that the solid regression line does not represent the data well, however, there is one data point that is not shown because it is off the scale of the graph. This point has a value of C_s equal to 0.275 mg/L and Γ equal to 1.359 $\mu\text{g/g}$, and when this point is included, the regression line shown is appropriate. The scale of the axis was not increased to include this data point so that the axes for all California desorption isotherm plots would remain identical allowing for visual comparison among different surfactant solution concentrations.

The partition coefficient did not appear to change appreciably, regardless of the surfactant concentration. Using the PCE, with only one exception, there was no evidence that the desorption isotherms were different from the adsorption isotherm for all surfactant concentrations studied. Also, there is no evidence of irreversibility for the experiment using water alone. The one exception is the experiment where a 0.25 percent surfactant solution was added for desorption. For this particular surfactant concentration, the partition coefficient showed an increase from 9.79 L/kg to 12.92 L/kg indicating an increase in sorption.

The clay mineralogy is again considered to explain these results. The clay fraction of the California soil contains a large percentage of

expandable clays, both montmorillonite and vermiculite. This results in a highly negative overall surface charge which is one reason for the high cation exchange capacity of the soil. This highly negatively charged surface results in electrostatic repulsion of the anionic surfactant and produces a relatively large diffuse double layer (Stumm and Morgan, 1981). It could also affect the nonionic surfactant because, although Tween-20 does not ionize, it is highly polar and the negative portion of the molecule could be repulsed. This repulsion was evident in the preliminary single point isotherm study that showed only 8.6 percent of the surfactant mixture adsorbed to the California soil. For a surface active agent, this is indeed a small extent of adsorption, particularly when considering that the California soil had by far the largest amount of surface area available.

It is plausible that the surfactant had little effect on the sorption of naphthalene because it was exposed to the soil after the naphthalene had already adsorbed and the surfactant was repulsed from the soil particle. The naphthalene on the surface of the soil was not proximate to the surfactant and, therefore, was not appreciably affected by its presence. The naphthalene simply responded as if there were no surfactant in the solution.

It is possible that the kinetics of the system play a role in these results in that the experimental conditions were such that the surfactant solution was only in contact with the contaminated soil for 48 hours. If the naphthalene had to diffuse from the surface of the soil a relatively greater distance to partition into the surfactant micelles, longer contact periods may have resulted in a positive surfactant effect.

Concentration of Surfactant For Use in Column Studies

In order to demonstrate how a surfactant improves the mobility of naphthalene in a flow-through column, the Charleston soil was the obvious soil of choice since results of the equilibrium studies showed that the surfactant would decrease the mobility of naphthalene in the Greenville soil and have negligible to negative effects for the California soil. Neither of the latter two soils would be suitable for a column study for the purposes intended.

Before initiating a column study it was necessary to determine the surfactant concentration to be used. As discussed previously, a minimum partition coefficient, and, hence, the greatest mobility, would occur at a surfactant solution concentration between 0.025 and 0.50 percent. To select an appropriate surfactant concentration, the log of the solution concentration versus the value of K_d was plotted. The result is shown in Figure 5.32. Both "solution concentration" and "concentration added" are plotted to emphasize the distinction between the two. The figure illustrates that there is a minimum K_d that lies between 0.025 and 0.50 percent solution concentration (or log percent surfactant solution of -1.6 to -0.3), but again not necessarily at 0.125 percent. Since the exact concentration to obtain a minimum K_d is not known, a decision was made to use a concentration represented by the average of the 0.025 and 0.50 values, which was 0.263 percent. For ease in solution preparation, this value was rounded off to 0.25 percent.

Before discussing the column studies, a comment must be made concerning the results of the present solubilization studies in relation to information presented in Chapter II. Valsaraj and Thibideaux (1989) derived an equation for estimating the retardation factor for surfactant

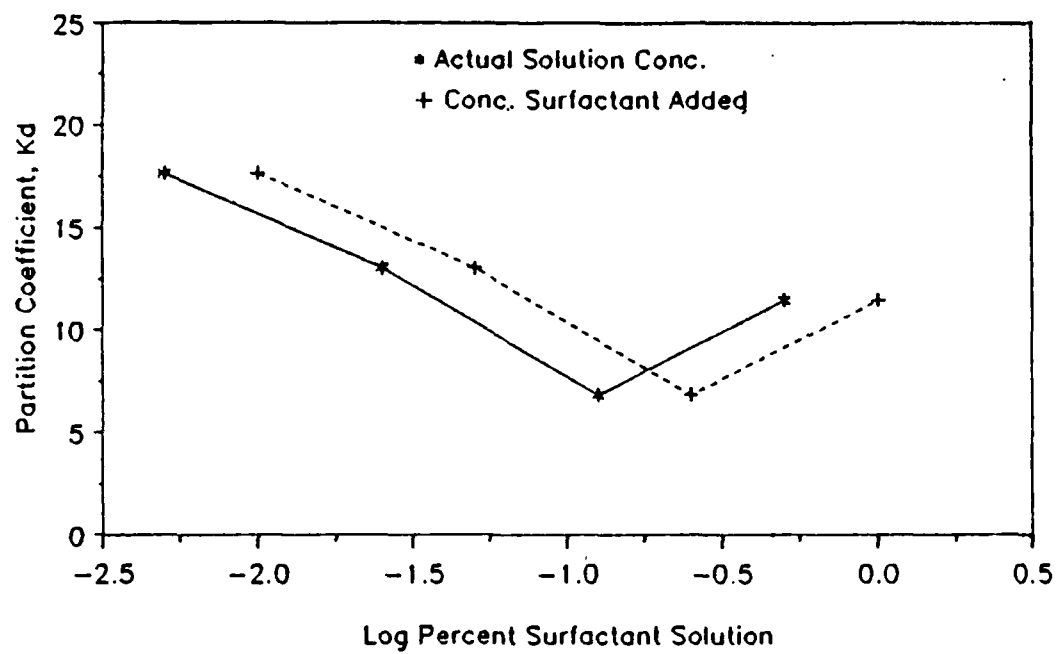


Figure 5.32. Plot of Partition Coefficient vs. Log Percent Surfactant Solution

micellar mediated transport of hydrophobic contaminants in groundwater.

$$R = 1 + \frac{K_{oc}[f_{oc}](1-n)\sigma_b/n}{1 + K_m v_w (C - CMC)} \quad (2.22)$$

They cautioned that this equation does not take into account surfactant sorption. Based on the results of the present investigations, this is a significant concern. Equation 2.22 predicts a decrease in retardation, or increase in mobility, any time the surfactant concentration is above the CMC. These experiments have shown that, based on surfactant interactions with the soil, the partition coefficient, and hence, retardation may be increased or decreased. One can only conclude that surfactant interactions with the soil must be considered in order to predict a surfactant's effect on the mobility of a contaminant.

Column Studies

Four column runs were conducted, where a "column run" is defined as an experiment involving two columns. The only planned difference among the four column runs was the flow rate used for naphthalene elution; 20, 40, 60 and 90 mL/hr. Each column run consisted of two phases. During the first phase naphthalene was adsorbed to the soil by applying a naphthalene solution to the column (loading). During the second phase naphthalene was desorbed, or eluted. This was accomplished by applying a surfactant solution to one column and a 0.01M CaCl₂ electrolyte solution to the other. The latter was used for comparison.

Adsorption Phase

The soil in each column was saturated with naphthalene as described in Chapter IV. The peristaltic pump was set to a flow rate of 60 mL per hour for this phase of the study, regardless of the planned elution

rate. Because all the columns were prepared identically, the adsorption of naphthalene on the soil for each column should have been similar. The experimental observations obtained during this phase included the time dependence of the column influent and effluent concentrations of naphthalene. The values of time were converted to the number of pore volumes processed by considering the flow rate and the pore volume within the column. These observations were used to develop normalized breakthrough curves as described in Chapter IV, where "breakthrough" is defined as the inflection point of the curve describing the concentration versus number of pore volumes eluted.

A typical breakthrough curve is shown in Figure 5.33. As previously discussed, the breakthrough curves were modeled as symmetrical ogives. SAS was used to determine the least square estimates for three parameters; (1) τ , which can be used to estimate the number of pore volumes at which breakthrough occurred as well as the retardation factor, (2) ϕ , which was a measure of dispersion, and (3) Ω , which represented the maximum concentration of naphthalene discharged from the column after breakthrough.

$$C = \frac{\Omega}{1 + \exp[\phi(\tau - N)]} \quad (4.23)$$

Equation 4.23 represented the data well, with R^2 exceeding 0.99 in all cases.

Because all the columns were prepared identically, the breakthrough response for each should have been very similar. Table 5.11 shows some of the physical characteristics for each column, as well as the parameter τ determined from the statistical analysis of the observations. This information indicates that the physical characteristics such as

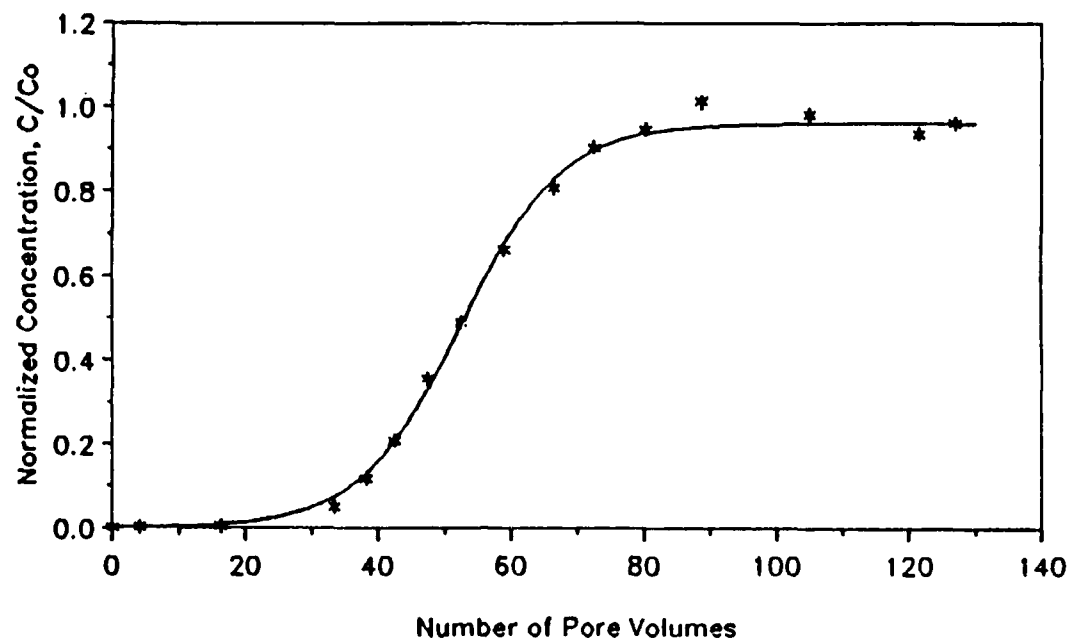


Figure 5.33. Normalized Naphthalene Breakthrough Curve (Run 1, Column 1)

Table 5.11. Summary of Column Characteristics and Calculated Partition Coefficients

Run/ Column	Column Length (cm)	Pore Volume (mL)	Porosity n	Bulk Soil Density (g/cm ³)	Average Flowrate (mL/h)	Average Flowrate (pv/h)	τ (pv)	K_d from Mass Adsorbed	K_d from Retardation Factor	K_d from Batch Experiments
1/1	10.7	23.04	0.44	1.86	56.20	2.44	52.44	17.40	12.17	16.84
1/2	10.7	23.04	0.44	1.86	54.70	2.37	48.27	17.80	11.18	16.84
2/1	10.9	24.03	0.44	1.86	57.89	2.41	36.23	14.57	8.33	16.84
2/2	10.9	24.03	0.44	1.86	57.89	2.41	37.10	16.36	8.54	16.84
3/1	10.8	23.53	0.44	1.86	58.98	2.51	43.76	17.97	10.12	16.84
3/2	10.8	23.53	0.44	1.86	58.09	2.47	40.25	15.47	9.28	16.84
4/1	10.7	23.04	0.44	1.86	56.03	2.43	40.45	15.14	9.33	16.84
4/2	10.7	23.04	0.44	1.86	54.89	2.38	40.37	14.90	9.31	16.84
Average	10.78	23.41			56.83	2.43	42.36	16.20	9.78	
Variation	0.01	0.17			2.22	0.00	26.97	1.64	1.51	
Std dev	0.08	0.41			1.49	0.04	5.19	1.28222	1.23	

Note: All loading of naphthalene was conducted at a flow rate set to 60 mL/h. The planned flow rates for subsequent elution were; Run 1 - 20 mL/h, Run 2 - 40 mL/h, Run 3 - 60 mL/h and Run 4 - 90 mL/h.

column lengths and pore volumes varied to a small degree. The differences, particularly among column runs, are attributed primarily to differences in packing the soil in the columns. In addition, even though the flow rate was always set to 60 mL/h, the actual rates varied from 54.89 to 58.98 mL/h.

The variability associated with the breakthrough points (τ) was more pronounced as compared with the variability of the physical parameters of the column, showing a standard deviation of 5.19 pore volumes. It was observed that relatively small differences in packing the column with soil could result in rather substantial differences in column performance.

The fact that a symmetrical ogive fits the data so well provides evidence as to the processes occurring within the column. Miller and Weber (1986) show similar responses for systems exhibiting linear sorption and local equilibrium, or first order rates of sorption. They relate that the breakthrough curve skews as diffusion processes become more important, with the inflection point of the curve occurring at lower concentrations with a slower approach to the maximum concentration eluted from the column.

Because of the symmetry observed, the response seen for these studies indicates that the majority of naphthalene sorption occurring within the column is to external surfaces rather than diffusion between expanded clay layers. This appeared reasonable considering the length of time required to complete the experiment, approximately 48 hours, as compared with the adsorption kinetic studies conducted for naphthalene on Charleston soil which showed that more than two weeks are required for a the batch system to closely approach equilibrium. Based on the

kinetic model and estimated parameters for the Charleston soil, only about 30 percent of the adsorption capacity is exhausted by 48 hours. Since the majority of the adsorption occurring in the initial phases of the kinetic study was rapid and attributed to external surface adsorption, it is likely that the sorption occurring within the column during a 48 hour period is similar. A consequence of this observation is that, since adsorption is primarily to external surfaces, elution of naphthalene from the column should occur more readily than if both external and diffusion-limited sorption processes were involved.

Comparison of Methods to Calculate the Partition Coefficient

The last three columns of Table 5.11 are presented to compare different methods of determining the partition coefficient. The value of K_d (from mass adsorbed) was determined by estimating the mass of naphthalene adsorbed to the soil in the column and dividing this by the mass of soil in the column, 75 g. An estimate of the mass of naphthalene adsorbed was obtained by graphically integrating the breakthrough curve as described in Chapter IV. The value of mass adsorbed per gram of soil then was divided by the value of C_0 . For example, from the first column of run number 1, the area between the breakthrough curve and C_0 was 428.9 mg/L·pv, the pore volume was 23.04 mL, and C_0 was 7.59 mg/L. From this information K_d was estimated by

$$K_d \text{ (L/kg)} = \frac{(428.9 \text{ mg/L} \cdot \text{pv})(23.04 \text{ mL/pv})}{(75 \text{ g})(7.59 \text{ mg/L})} = 17.4 \text{ L/kg} \quad (5.6)$$

The K_d determined from the retardation factor was calculated using the definition of the retardation factor as presented in Chapter II.

$$R = \tau = 1 + \sigma_b K_d / n \quad (2.21)$$

where σ_b is the soil bulk density and n is the porosity. This definition is based on the assumption of linear and reversible sorption along with local equilibrium. Two of these conditions are not fulfilled precisely when applied in this circumstance. First, the equilibrium studies showed that there was a slight extent of irreversible sorption. Secondly, as previously discussed, local equilibrium most likely is not a fully applicable assumption for these column experiments due to the relatively short equilibration times. Accordingly, the values of K_d reported are subject to these limitations. Solving for K_d using Equation 2.21 yielded

$$K_d (\mu\text{g/g}) = [(\tau - 1) \times n] / \sigma_b . \quad (5.7)$$

The value reported for K_d obtained from the batch equilibrium data in Table 5.11 is 16.84 L/kg instead of the calculated value of 19.47 L/kg. This was done because the batch equilibrium studies were conducted using the fraction of soil having particle diameters less than 250 μm , whereas the soil fraction having particle sizes less than 2.0 mm was used for the column studies. Using the grain size distribution given in Table 5.1, it was calculated that soil particles having diameters less than 250 μm represent 86.5 percent of the total mass of soil. Assuming that the great majority of sorption occurs on the fraction less than 250 μm , a reasonable correction can be made to estimate the partition coefficient for the soil fraction containing particles less than 2.0 mm where

$$K_d (\mu\text{g/g}) = K_{d(250\mu\text{m})} \times (0.865) . \quad (5.8)$$

A comparison of the three methods used for determining values of K_d shows that the average K_d determined from the masses of naphthalene adsorbed to the soil in the column compares favorably with the K_d

determined from the batch equilibrium studies. The K_d values determined from the retardation factor, however were consistently lower. One factor that must be considered is related to access to sorbent sites. In the batch studies the system was well-mixed throughout the contact period. Packed soil in the column restricts naphthalene from coming into contact with portions of the soil due to channeling, and this lack of access to sorbent sites results in a lesser extent of adsorption.

Channeling may also influence the effective pore volume of the column due to zones of mobile and immobile fluid. Because the immobile fluid does not flow and occupies a percentage of the calculated pore volume, the fluid that is moving appears to do so based upon a reduced porosity. This results in an effective pore volume less than that calculated based on the actual porosity of the soil. Using a value for effective pore volumes eluted on the horizontal axis of Figure 5.33 instead of calculated pore volumes eluted would have the effect of shifting the breakthrough curve to the right. This would result in a larger value of τ , and, hence, a larger K_d , closer to the values determined by the other methods. A tracer study to determine the effective pore volume was not accomplished as part of these investigations, and, therefore, a correction to account for effective pore volume could not be made.

Nonetheless, the observation of lower calculated K_d 's determined from using the retardation factor is consistent with the previous discussion concerning the period of time the experiment was conducted. Schwarzenbach and Westall (1981) reported that compounds are retained in a flow-through column less effectively at higher flow rates because the contact time between the soil and solution is decreased. This does not

allow the system to approach equilibrium, resulting in less of the solute adsorbing onto the soil. Because less mass is adsorbed, the compound is detected in the effluent at fewer pore volumes passed than if the flow rates (retention times) were lower. This has the effect of shifting the breakthrough curve to the left, and, hence, a lower value of τ , or, the retardation factor. Clearly, from Equation 5.7, a reduction in τ results in a lower estimate for K_d .

As previously discussed, the kinetic studies conducted with naphthalene and Charleston soil showed that only about 30 percent of the soils equilibrium sorption capacity would be exhausted by the 48 hour retention time used for these column studies, however, the 30 percent value is influenced by the kinetics of clay expansion which was not a factor for the column studies. Based on this, one would expect the partition coefficient calculated from the column studies to be at least 30 percent of the partition coefficient determined from the batch equilibrium studies ($16.84 \times 0.3 = 5.85 \text{ L/kg}$), but more likely greater than 30 percent. The partition coefficients calculated from the column studies are between 5.85 L/kg and the K_d calculated from the equilibrium sorption studies and appear consistent considering the kinetics of naphthalene adsorption as well as the kinetics of clay expansion.

Since the estimate of the mass of naphthalene adsorbed to the soil in the column is also affected by the shift in the breakthrough curve, the question arises as to why, then, are the values of K_d determined similar to Equation 5.6 not also lower? Intuitively, as the breakthrough curve shifts to the left, the area between the curve and C_0 should decrease resulting in a decrease in the partition coefficient. The reason the decreases were not detected is most likely due to an

artifact of the experimental method. As discussed in Chapter IV, the influent naphthalene concentration could not be monitored throughout the experiment, and an average value for readings taken at the beginning and the end of the adsorption phase was used as estimates for C_0 . This method probably over-estimated the actual mean value of C_0 resulting in a greater amount of area between the breakthrough curve and C_0 than would have occurred with lower values of C_0 . In the estimation of K_d , then, the mass of naphthalene adsorbed used for the calculation was greater than the actual value. In contrast, the over-estimation of C_0 had no effect on the value of K_d determined from the retardation factor because C_0 is not considered using this method.

Another observation that indicated the value of C_0 used for these studies may be over-estimated came as a result of the naphthalene breakthrough curves. The statistical analysis of each breakthrough curve indicated that the naphthalene concentration after breakthrough never reached a value of C_0 , in some instances reaching only 82 percent of C_0 (data in Appendix F). In ideal systems, these types of responses are indicative of a loss of compounds by processes other than adsorption such as a chemical or biological transformation. However, considering that naphthalene is relatively non-reactive and the soils were sterilized, an 18 percent loss of naphthalene in the amount of time these experiments were conducted (approximately 48 hours), is not likely.

The most likely explanation for this response is that the approach of naphthalene concentration to C_0 after breakthrough was so slow it could not be determined by the method of analysis. In most cases, toward the end of the experiment, the influent naphthalene concentration was lower than at the beginning due to volatilization of naphthalene in the

10 L reservoir. Since the maximum naphthalene concentration after breakthrough primarily is a function of the influent concentration at that time, the average calculated C_0 may never occur. These anomalies make interpretation of the data very difficult and must be taken into consideration before drawing any conclusions.

When considering the three methods discussed for determining the value of K_d for use in the field, Relyea (1982) recommended using the method that involved the retardation factor, since this most closely simulated actual conditions when the flow rate in the column was similar to the flow rate in the field. For engineering purposes, it may be best to use the most conservative value for a specific circumstance. For example, the smallest K_d (greatest mobility) might be used when estimating how far the leading edge of a contaminant plume has migrated. Likewise, the largest K_d (lowest mobility) might be used for estimating the trailing edge or when estimating contaminant movement in a pump and treat system.

Naphthalene Elution from Columns

For each column run, one column was eluted with water and the other with surfactant solution. The only planned difference among column runs was the elution flow rate. The pump flow rates used were 20, 40, 60 and 90 mL/h. These rates were chosen because they resulted in flow velocities typical of those observed when remediating an aquifer by the pump and treat process.

Before discussing the results of the column runs, a comment about the 60 mL/h run should be made. Approximately halfway through the loading portion of this run, the fluorescent spectrometer malfunctioned and

became unusable. The loading and elution phases of the experiment were continued and each three mL sample was saved by introducing it into a 20 mL scintillation vial and storing it in a refrigerator at 3°C. Approximately two weeks later the spectrometer was repaired and the stored samples were analyzed after being allowed to warm to room temperature. Although steps were taken to minimize volatilization of naphthalene, it is suspected that some may have occurred resulting in determinations of naphthalene concentrations that were slightly lower than would have been the case had the samples been analyzed immediately.

Elution Curves

The results of eluting naphthalene from columns were normalized by manipulating the data to produce curves of C/C_0 versus number pore volumes eluted (elution curve) and M_e/M_a (mass eluted/mass adsorbed) versus number pore volumes eluted (cumulative mass eluted curve). The reason for normalizing these curves was to be able to compare results between column runs where operating conditions were not exactly the same.

The results of these experiments are presented by the C/C_0 versus pore volumes eluted curves shown in Figures 5.34 through 5.37 and the M_e/M_a versus number of pore volumes eluted curves shown in Figures 5.38 through 5.41. The corresponding data is given in Appendix F. In order to make comparisons of the efficiencies of naphthalene removal, each normalized mass eluted curve was modeled. For the columns eluted with water, an exponential function similar to that used for the kinetic studies was applied. This model fit the data very well with R^2 greater than 0.99 for all columns. For the columns eluted with surfactant solutions, however, the initial elution response was approximately linear

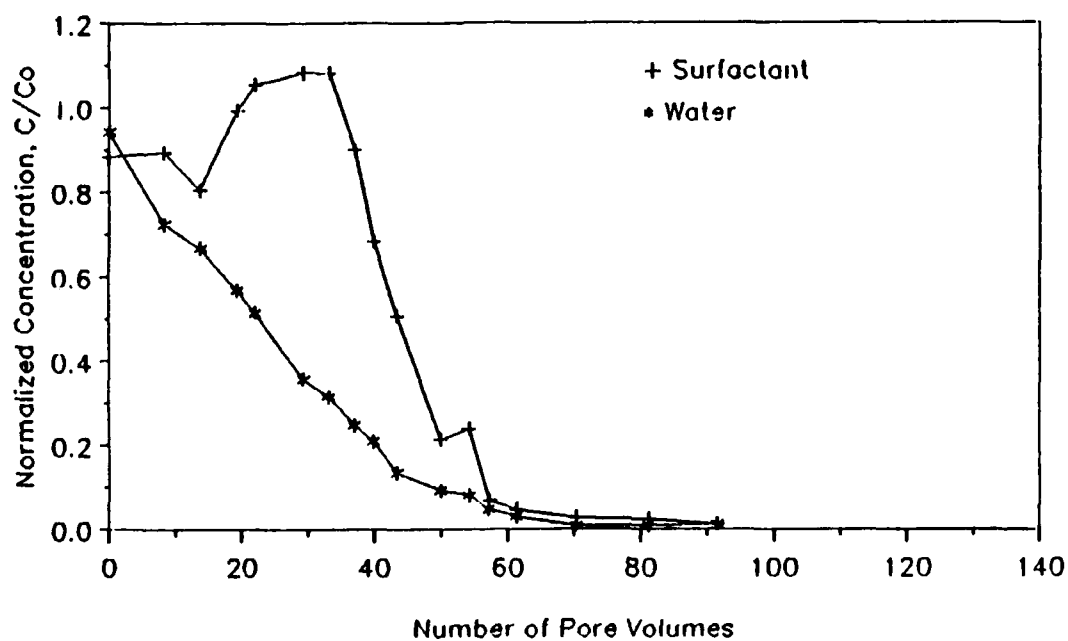


Figure 5.34. Normalized Naphthalene Elution Curve at a Flow Rate Set to 20 mL/h

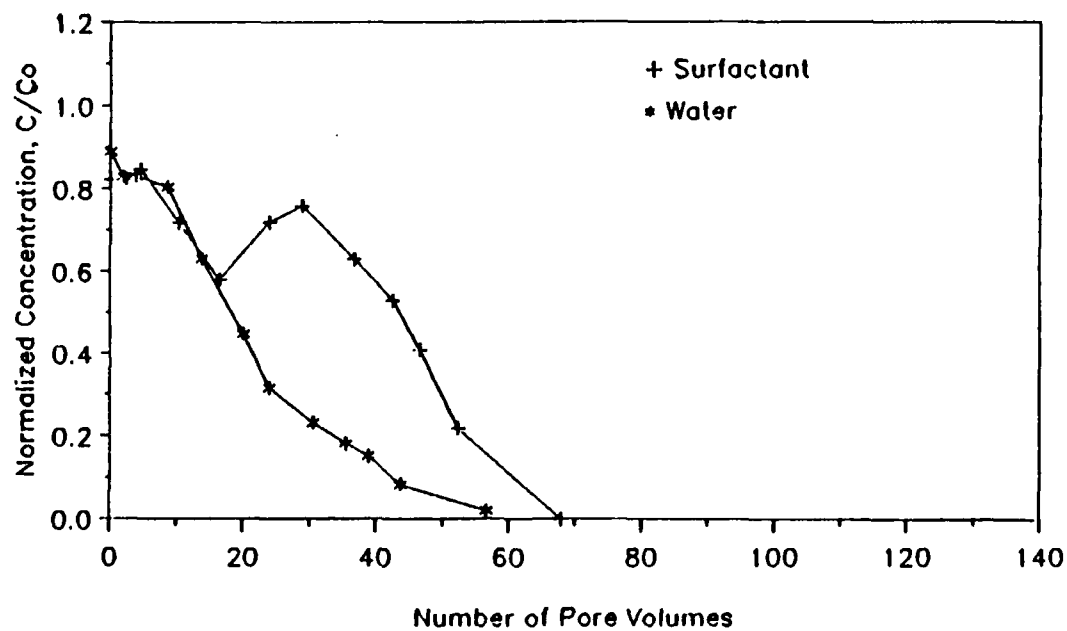


Figure 5.35. Normalized Naphthalene Elution Curve at a Flow Rate Set to 40 mL/h

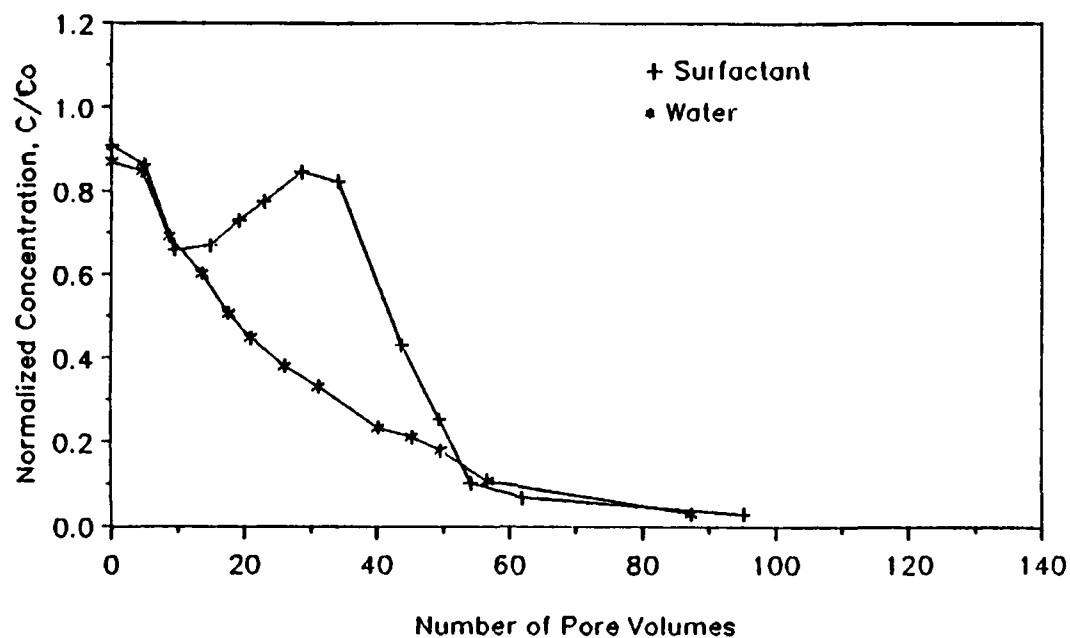


Figure 5.36. Normalized Naphthalene Elution Curve at a Flow Rate Set to 60 mL/h

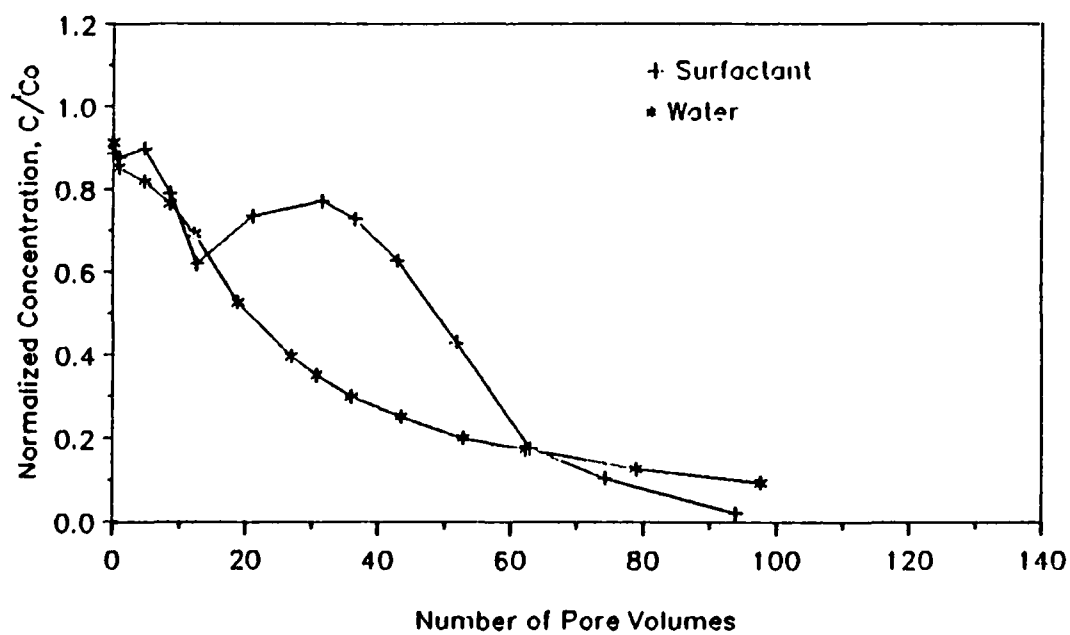


Figure 5.37. Normalized Naphthalene Elution Curve at a Flow Rate Set to 90 mL/h

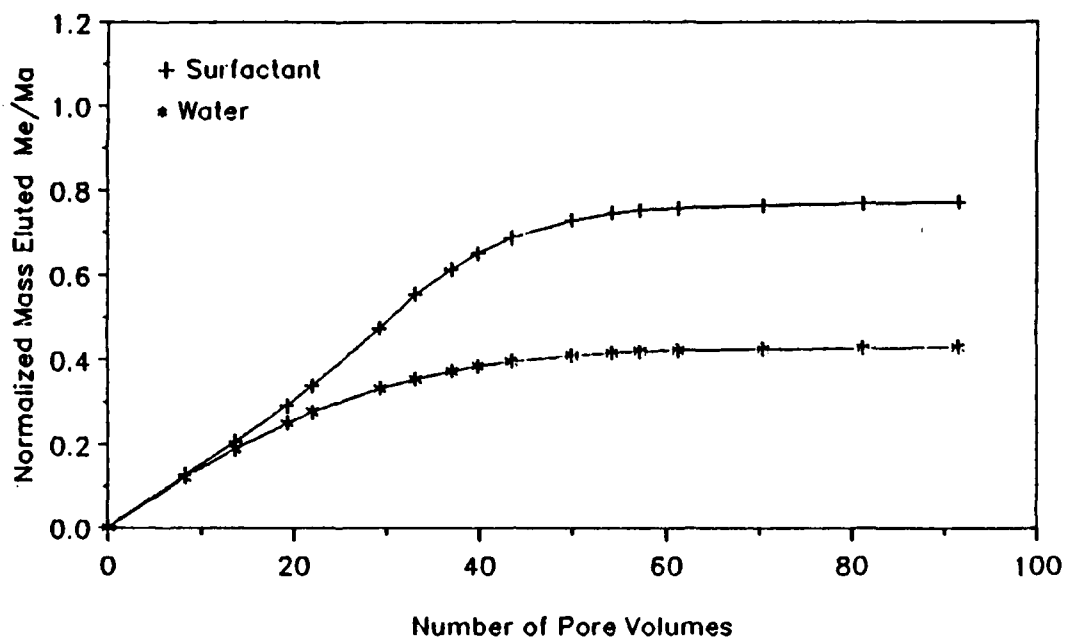


Figure 5.38. Cumulative Normalized Mass Naphthalene Removed Curve at a Flow Rate set to 20 mL/h

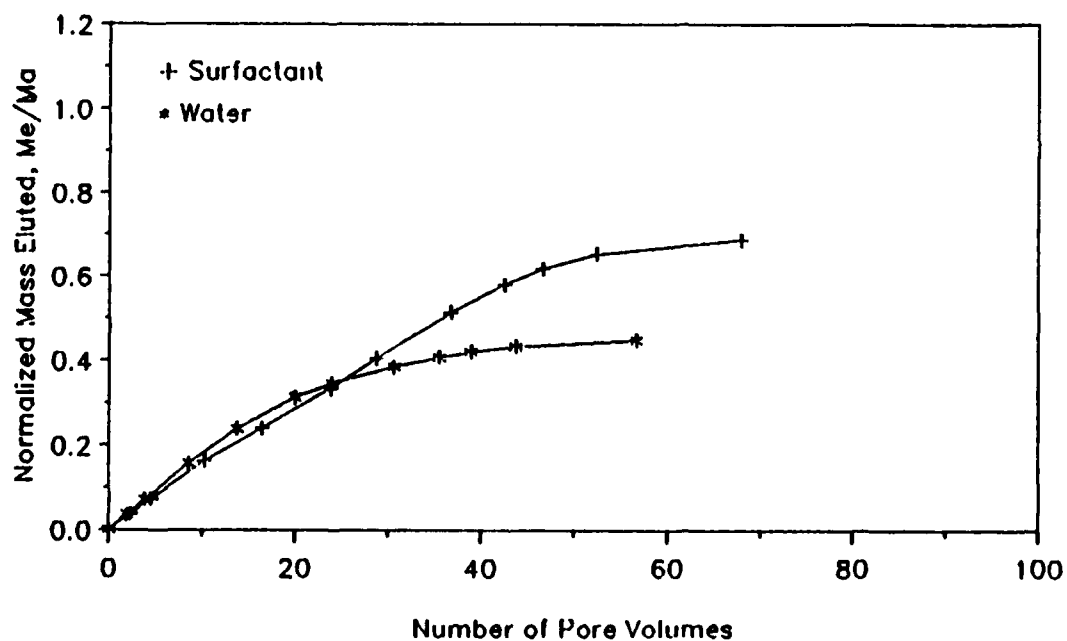


Figure 5.39. Cumulative Normalized Mass Naphthalene Removed Curve at a Flow Rate set to 40 mL/h

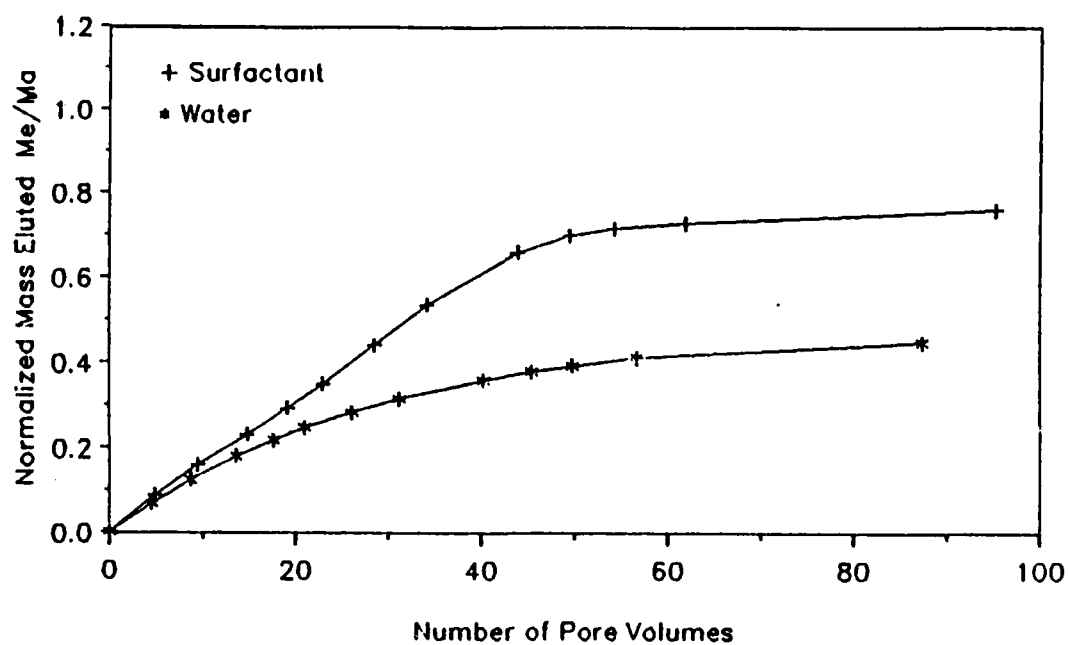


Figure 5.40. Cumulative Normalized Mass Naphthalene Removed Curve at a Flow Rate set to 60 mL/h

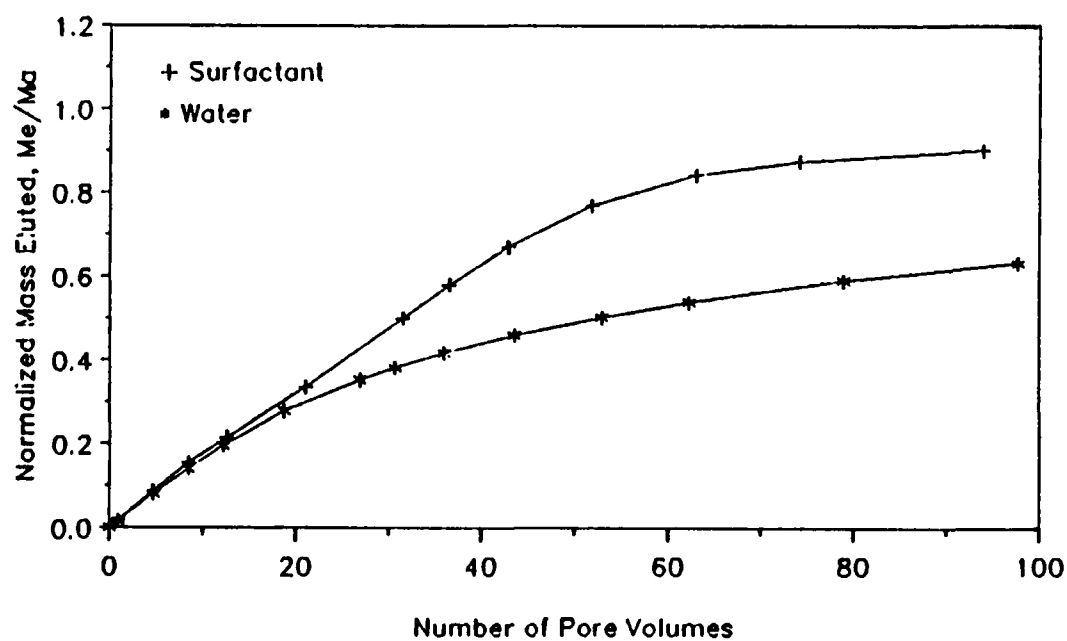


Figure 5.41. Cumulative Normalized Mass Naphthalene Removed Curve at a Flow Rate set to 90 mL/h

followed by an exponential type of rise. A model was developed to describe the initial data points as a straight line and those that followed by an exponential function. The model is of the form:

$$M_e/M_a = Z(\epsilon_1 + \epsilon_2 PV) + (1-Z)(\epsilon_3 - \epsilon_4 e^{IPV}) \quad (5.9)$$

where ϵ_1 and ϵ_2 are statistical parameters for the linear portion of the curve, and ϵ_3 , ϵ_4 and Z are statistical parameters for the exponential function. The value of Z is set to 1 if the data point is on the linear trace, and zero if the data point is on the exponential portion of the curve. SAS was used to fit the model to the data for the eight experimental elution curves obtained. The estimate of the parameter ϵ_3 was particularly useful to compare mass removals because this parameter represents the asymptote of the function. Plots of the fitted models are presented in Appendix G, whereas the solid lines in Figures 5.38 through 5.41 simply connect data points.

Naphthalene Elution by Water

The results of eluting naphthalene from the soil columns with water (Figures 5.34 through 5.41) show a first order decay type of response, typical of those reported in the literature. For example, Talbert and Fletchall (1965) reported similar curves for triazines being eluted from columns containing silty clay loam soils. The same response was reported by Miller and Weber (1986) for Lindane as the contaminant desorbed from soil. This type of response indicates that sorption equilibrium is not attained for this column system. The elution response when equilibrium is attained would be the mirror image of the loading breakthrough curve. For example, referencing Figure 5.33, the elution curve under equilibrium conditions would initially remain close to 1.0 at low

numbers of pore volumes passed. As the number of pore volumes passed increases, the curve then would decrease, taking the form of a symmetrical ogive asymptotic to zero. The inflection point of the curve would occur at the same number of pore volumes passed as the inflection point for the loading breakthrough curve. Since the responses seen for these studies do not exhibit the elution response described above, it is clear that equilibrium is not attained, and sorption kinetics influence the results.

A comparison of the elution of naphthalene with water alone at various flow rates was made to determine whether any trends could be noted relating the magnitude of the flow rates and efficiencies of removal. The plots of C/C_0 versus PV for water elution were taken from Figures 5.34 through 5.37 and plotted together as shown in Figure 5.42. Similarly, the plots of M_e/M_a for water elution were taken from Figures 5.38 through 5.41 and are plotted on Figure 5.43. A summary of the calculated asymptotes for the M_e/M_a curves is given in Table 5.12. The asymptotic values indicate that less than half of the mass of naphthalene adsorbed to the soil is eluted, and appears inconsistent with the relatively rapid desorption rates reported for the kinetic desorption study. However, as previously discussed, the rates reported were most likely for the labile fraction of naphthalene adsorbed. Considering this, the results are, in fact, consistent. The naphthalene initially eluted from the column is the labile fraction. At greater numbers of pore volumes passed, the mass removal rates, or, slopes of the M_e/M_a curves, decrease significantly and represent the slow elution of the nonlabile fraction.

The elution curves in Figure 5.42 show that elution was similar at all flow rates using water alone with the exception of the column eluted

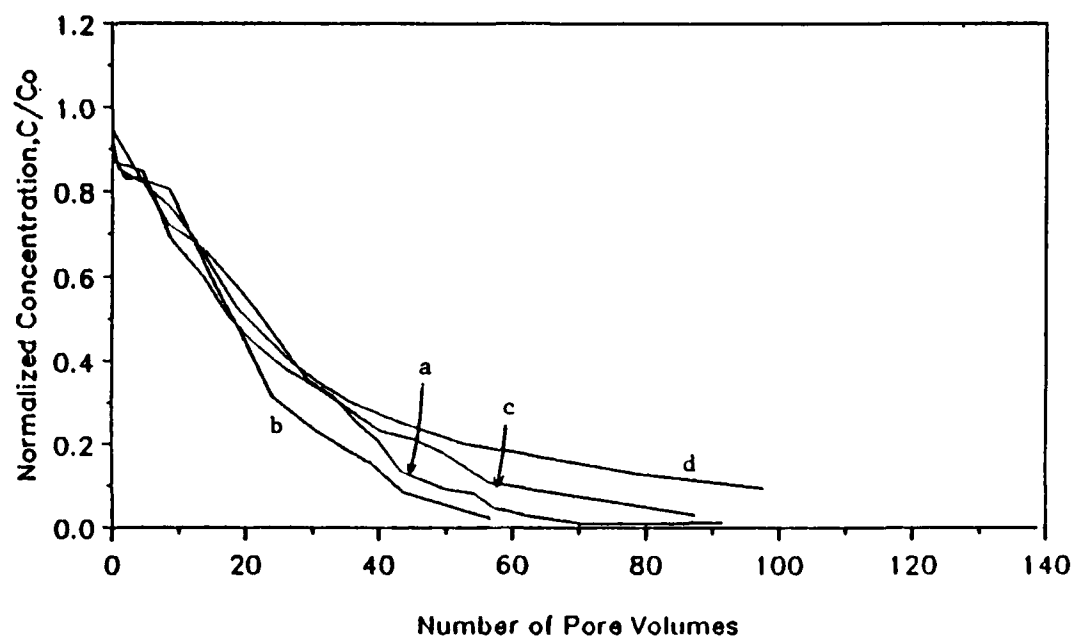


Figure 5.42. Normalized Naphthalene Elution Curves Using Water Alone at Four Different Flow Rates; (a) 20 mL/h, (b) 40 mL/h, (c) 60 mL/h, (d) and 90 mL/h

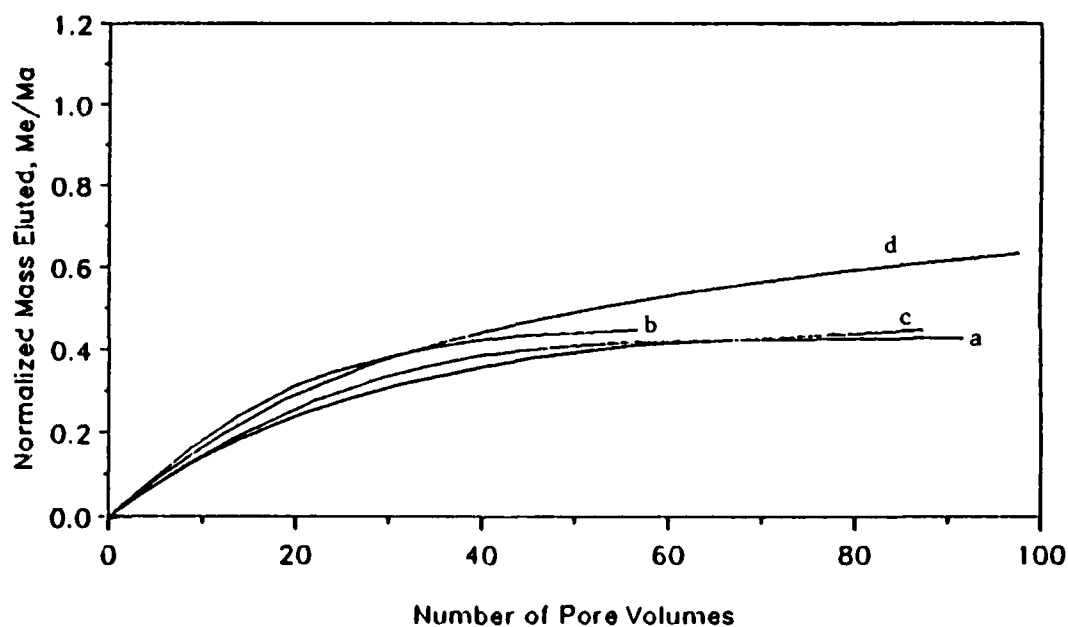


Figure 5.43. Cumulative Normalized Mass Naphthalene Eluted Curves Using Water Alone at Four Different Flow Rates; (a) 20 mL/h, (b) 40 mL/h, (c) 60 mL/h, and (d) 90 mL/h

Table 5.12. Values for Asymptotes Determined from Statistical Analysis of M_w/M_n vs. PV Curves for Elution by Water Alone at Different Flow Rates, and Reynolds Numbers.

Elution Rate (mL/hr)	Asymptotic Value (ϵ_3)	95 Percent Interval Estimate	N_{Re}
20	0.450	0.436 - 0.463	3×10^{-3}
40	0.488	0.468 - 0.509	6×10^{-3}
60	0.472	0.467 - 0.476	9×10^{-3}
90	0.664	0.649 - 0.680	13×10^{-3}

at a flow rate of 90 mL/h which showed higher concentrations of naphthalene after those of the of the other three experiments had approached a trace level. This affected the M_o/M_a curves shown in Figure 5.43. A summary of the values of the asymptotes for these curves is given in Table 5.12. Although the asymptotic values for the column runs conducted at 20, 40 and 60 mL/h all were within 5 percent, the column run conducted at 90 mL/h showed a much greater value indicating a greater extent of removal of the mass of naphthalene.

To determine whether this response may have been influenced by a transition from laminar to turbulent flow, the Reynolds number, NR_o , was calculated. For flow of fluid through porous media, the Reynolds number is calculated by (Peavy et al., 1985)

$$NR_o = \frac{\phi_r \sigma V d}{\mu} \quad (5.10)$$

where

ϕ_r = shape factor (approximately 0.7 for soil),

σ = density of water (998.2 kg/m³),

V = interstitial velocity (m/s),

d = diameter of particles (m),

μ = dynamic viscosity of water (1.002×10^{-3}) N·s/m².

The value used for the particle diameter was an average diameter calculated from the grain size distribution to be 1.65×10^{-4} m. All calculated Reynolds numbers were very low, as shown in Table 5.12, indicating laminar flow prevailed for all studies. Consequently, it is not likely that a change in the flow regime influenced the column run conducted at 90 mL/h.

Another potential explanation for the improved extent of removal observed at the 90 mL/h flowrate related to boundary layer effects.

Since the naphthalene must diffuse from the soil surface through this boundary layer in order to partition into a micelle in solution, a reduction in the thickness of the boundary layer would improve mass transfer. To determine the effect of the various flow rates on mass transfer, mass transfer coefficients for each flow rate were calculated. Crittenden (1986) related an empirical relationship to determine mass transfer coefficients, k_r , where

$$k_r = 1.09v(N_{re}Sc)^{-2/3} \quad (5.11)$$

In Equation 5.11, v is the interstitial velocity and Sc is defined as the Schmidt number

$$Sc = \frac{\mu}{D_{ab}\sigma} \quad (5.12)$$

where μ is the dynamic viscosity of the fluid, D_{ab} is the diffusivity of compound a in b, and σ is the liquid density. An estimate of the diffusivity was calculated by a method described by Wilke and Chang (1955) in which

$$D_{ab} = 7.4 \times 10^{-8} \frac{TxM^{1/2}}{\mu V_b^{0.6}} \quad (5.13)$$

where

T = absolute temperature,

x = 2.6 for water,

M = molecular weight of water,

μ = viscosity of water,

V_b = molecular volume for the solute at its boiling point.

For naphthalene and water, the diffusivity was calculated to be 1.6×10^{-6} cm²/s. Substituting this value into Equation 5.12, and the resulting

Schmidt number into Equation 5.13 resulted in calculated mass transfer coefficients for increasing flow rates of 0.0117, 0.0148, 0.0169 and 0.0194 cm/s, or increasing with the cube root of the velocity. If mass transfer were a factor, then, an increase in the rate of mass desorbed would have been detected for each increase in flow rate. The rates of mass desorbed are represented by the slopes of the M_0/M_A versus number of pore volumes curves shown in Figure 5.43, and this trend is not evident. In fact, particularly for a number of pore volumes less than 20, the rates of mass removal appear to be similar regardless of the flow rate used. This serves to indicate that mass transfer was not a factor.

Based on the considerations described above, it was concluded that there may have been a systematic error associated with the column run conducted at 90 mL/h. The naphthalene concentrations in the latter portions of the experiment were higher than would be expected, and this occurred for the elution with surfactant as well. It is plausible that these higher concentrations resulted from an error associated with the standard naphthalene solution. The concentration in the standard solution may not have remained constant during the entire column run. If the cap was not tightened adequately, or the septum developed a leak, the concentration may have decreased due to volatilization of naphthalene. The effect of standardizing the fluorescent spectrometer with this solution would result in determinations of effluent naphthalene concentrations higher than was actually the case. Since volatilization of naphthalene from the standard solution is time dependent, the errors introduced would be more pronounced toward the end of the experiment producing the results seen for the column run conducted at 90 mL/h.

The conclusion drawn from these experiments is that variations in flow rate had minimal effect on the efficiency of extracting naphthalene

from the soil for the conditions under which the experiments were conducted. For engineering applications, particularly where nonspecific surface interactions are responsible for adsorption, the flow rate would not influence the efficiency of contaminant extraction. Greater pumping rates would decrease the time required to remediate the aquifer. When kinetic factors influence the efficiency of contaminant extraction, however, different pumping strategies must be investigated.

Naphthalene Elution by Surfactant Solution

The C/C_0 versus pore volumes eluted curves for surfactant solutions are shown in Figures 5.34 through 5.37. These curves were combined in Figure 5.44 for comparison purposes. The data plotted in Figure 5.44 shows an initial decrease in naphthalene concentration which is followed by an increase in concentration for columns all eluted with surfactant solutions. In all of the experiments, this increase in concentration peaked at approximately 30 pore volumes eluted. The initial decrease is similar to the response noted for the elution with water as shown in Figures 5.32 through 5.35. This would be expected at the outset of the elution phase of the experiment when only water is eluting from the column. If the surfactant did not adsorb to the soil, the surfactant as well as solubilized naphthalene would appear in the effluent after approximately one pore volume, or even less when channeling and dispersion effects are considered. However, the equilibrium surfactant sorption studies showed that surfactant does adsorb, and, consequently, its flow through the soil is retarded. The increase in naphthalene solubilization, peaking at approximately 30 pore volumes, is due to the surfactant "breaking through" and carrying solubilized naphthalene with it.

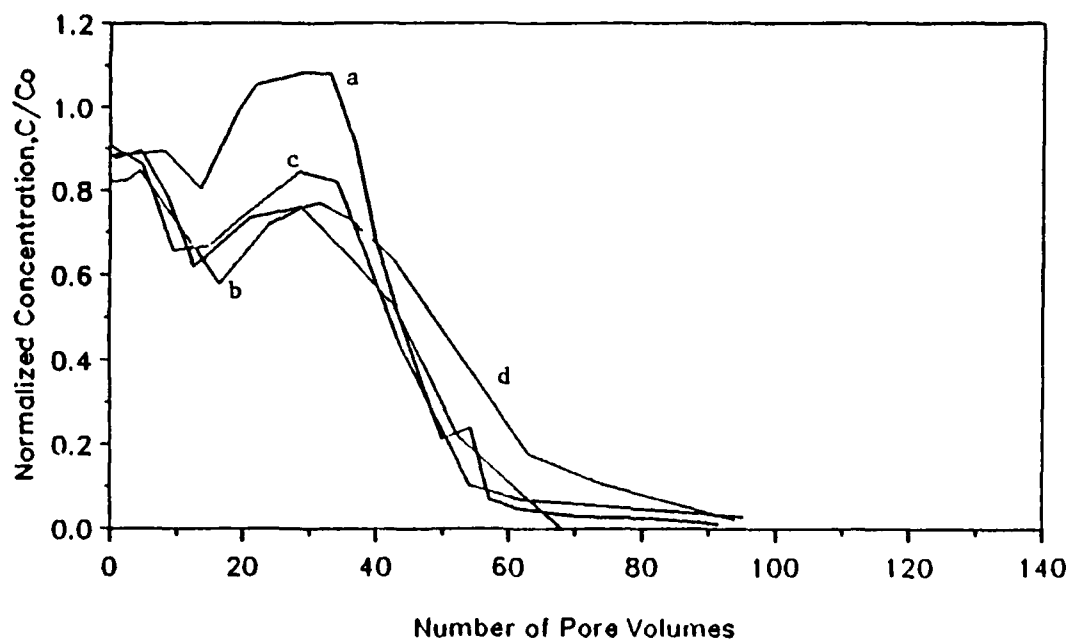


Figure 5.44. Normalized Naphthalene Elution Curves Using Surfactant solution at Four Different Flow Rates; (a) 20 mL/h, (b) 40 mL/h, (c) 60 mL/h, and (d) 90 mL/h

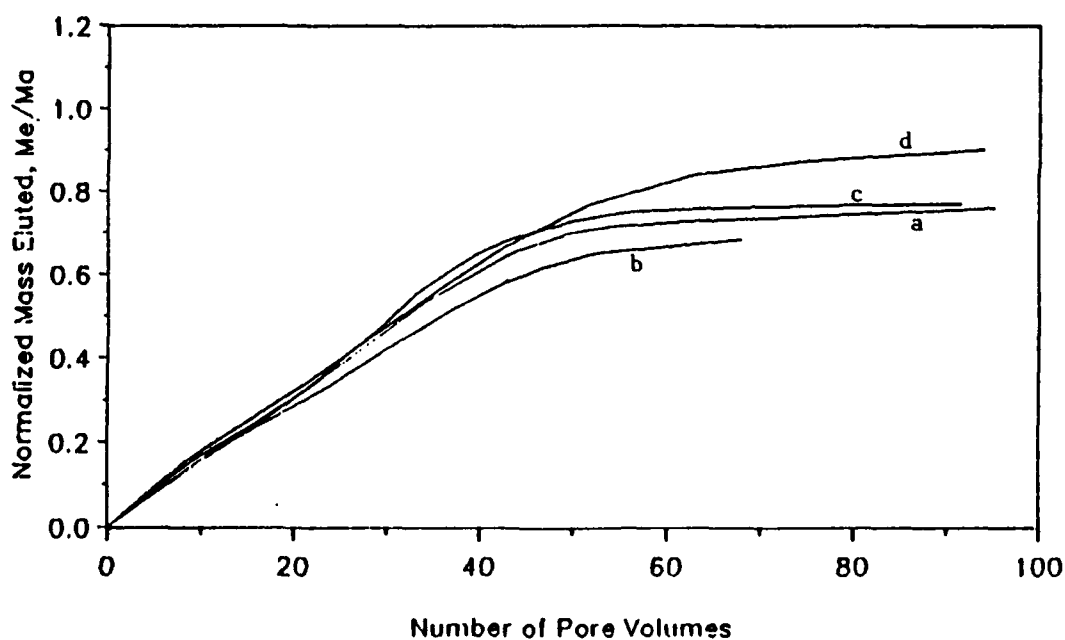


Figure 5.45. Cumulative Normalized Mass Naphthalene Eluted Curves Using Surfactant Solution at Four Different Flow Rates; (a) 20 mL/h, (b) 40 mL/h, (c) 60 mL/h, and (d) 90 mL/h

Since the mass of naphthalene eluted can be calculated from integrating the C/C_0 curve versus pore volume curve, the peaking effect increases the amount of area under the curve as compared with the water elution curves. It is evident that this increases the mass of naphthalene removed as compared with water alone.

The responses shown on Figure 5.44 are very similar for the columns when eluted at 40, 60 and 90 mL/h. As discussed previously, the experiment conducted at 90 mL/h showed higher concentrations in the latter stages of the experiment similar to the elution with water alone. The column eluted at 20 mL/h has a much higher peak. If there were a trend that the peaks increased as the flow rates decreased, it would indicate that a rate process may be affecting the system. However, this trend was not noted for the other columns at the various elution rates. Calculations of masses adsorbed by the soils in the columns indicated that the column run conducted at 20 mL/h had by far the greatest amount of mass adsorbed, 9.97 mg, as compared with the other three runs which adsorbed 6.85, 6.69 and 7.47 mg for the runs conducted at 40, 60 and 90 mL/h, respectively. It is likely that the higher peak for the column study conducted at 20 mL/h is due to the fact that there was more naphthalene available to solubilize. The effect of this, however, is minimized for the normalized mass eluted curves (Figure 5.45), because the amount of mass adsorbed is used to normalize the data.

Normalized mass eluted curves for surfactant solutions plotted in Figures 5.38 through 5.41 were re-plotted together as shown in Figure 5.45. The results of a statistical analysis once again provided asymptotic values with which to compare efficiencies of the removal of mass of naphthalene among the various flow rates, as well as to compare

efficiencies between water and surfactant solutions. Table 5.13 provides the values of the asymptotes, and the percent improvement in the effectiveness of the surfactant solution to remove naphthalene when compared to the elution with water alone.

Table 5.13. Values for Asymptotes Determined from Statistical Analysis of M_e/M_a vs. PV Curves for Elution by Surfactants at Different Flow Rates, and Percent Increases in Effectiveness over Water Alone

Elution Rate (mL/hr)	Asymptotic Value (ϵ_s)	95 Percent Interval Estimate	% Increase Compared with Water Alone
20	0.773	0.764 - 0.781	71 %
40	0.703	0.657 - 0.730	44 %
60	0.757	0.743 - 0.771	60 %
90	0.917	0.893 - 0.940	38 %

The asymptotic values given in Table 5.13 show a trend similar to the one seen for the elutions with water alone. In this case, the values of the asymptotes are within 7 percent of each other for the experiments conducted at flow rates of 20, 40 and 60 mL/h and the curves shown in Figure 5.45 appear to converge as the numbers of pore volumes increases. The experiment conducted at 90 mL/h showed a much greater asymptotic value. The explanation of the increase in mass removed for the 90 mL/h run is exactly the same as that previously discussed for the elution with water alone.

The percent increase in naphthalene removal when compared to the water elution at the same flow rate showed a substantial benefit when

using the surfactant solution. This can also be seen in Figures 5.38 through 5.41. The percent increase does show variability among column runs at different flow rates, with data in Table 5.13 ranging from a 38 to a 71 percent increase, however, there does not appear to be a trend with respect to flow rates. Since the only planned difference among column runs was the flow rate, this variability must be attributed to variability in column packing, experimental errors and the method of analysis.

To this point, the term "efficiency" has been used with respect to the amount of mass of naphthalene removed from the soil as compared with the amount of mass that had adsorbed. Another measure of efficiency, particularly from an engineering perspective, is how the use of surfactant solutions affects the length of time required for an aquifer restoration process. In order to give an indication of the time savings that might be gained, the modeled cumulative normalized naphthalene elution curves were used (Appendix G). The mathematics of the model is such that a horizontal asymptote is determined. According to the model, then, the cumulative mass of naphthalene removed would never exceed the asymptotic values given in Tables 5.12 and 5.13. In reality, however, the mass of naphthalene represented by that above the asymptote does not stay in the aquifer forever; it continues to elute, but at a very slow rate.

To estimate the number of pore volumes required to obtain, for example, removal of 90 percent of the naphthalene, the model cannot be used "as is" because 90 percent is above the value of the asymptote in nearly all cases. To make a rational estimate for these values, it was decided to obtain the slope of the curve (mass removal rate) within the

range of the data and where all the curves exhibited a slow approach to their asymptotic value. An assumption was then made that this very small removal rate would remain fairly constant; i.e., linear until all of the naphthalene was removed. It is recognized that this is a non-conservative assumption because the rates actually continue to decrease, and this must be considered when interpreting the results. From a visual inspection of the curves, and the range of pore volumes from which the data was obtained, it was decided that the slope of each curve at 70 pore volumes would be used to obtain mass removal rates for comparing elutions with water and surfactants.

To obtain the slopes, the exponential model for the elutions with water and the exponential portion of the model used for elution with surfactants were differentiated with respect to the number of pore volumes. These mathematical expressions, representing the slopes of each curve, were used with the model parameters determined from SAS to calculate the rates of mass of naphthalene removal at 70 pore volumes. Based on this calculated rate and the mass of naphthalene already removed at 70 pore volumes, an estimate was obtained for the number of pore volumes required to pass in order to obtain cumulative normalized naphthalene removals of 0.90, 0.95 and 0.99. The results of this analysis are presented in Table 5.14.

Considering that the estimates of the rates of naphthalene removal are conservative estimates, the number of pore volumes required to attain these extents of naphthalene removal is staggering, particularly for the higher removal rates. For example, if a contaminant plume had spread in an aquifer with a porosity of 0.35 to cover a 50 x 50 m area, and the depth of the contamination was 10 m, one pore volume would be

Table 5.14. Results of Analysis to Determine the Number of Pore Volumes Eluted to Produce Removals of Total Naphthalene of 0.90, 0.95 and 0.99

Flow Rate (mL/h)	Solution	Model Parameters			M_e/M_a at 70 Pore Volumes	Slope ($\times 10^{-4}$) (pv^{-1})	Pore Volumes for Removal of M_e/M_a		
		ϵ_3	Σ	ϵ_3			0.90	0.95	0.99
20	Water	0.45	0.045	N/A	0.430	8.89	599	655	700
20	Surf.	0.77	0.093	4.177	0.766	8.60	268	341	400
40	Water	0.49	0.049	N/A	0.473	7.67	627	692	744
40	Surf.	0.70	0.080	3.555	0.689	10.70	402	437	465
60	Water	0.47	0.035	N/A	0.432	14.13	402	437	465
60	Surf.	0.76	0.082	3.597	0.745	9.59	231	284	325
90	Water	0.66	0.028	N/A	0.569	26.50	195	214	229
90	Surf.	0.92	0.054	2.455	0.861	30.1	83	100	113

8750 m³. At a typical pumping rate of 750 L/min, one pore volume would be pumped in approximately 6.1 days. From Table 5.14, the number of pore volumes required to be pumped to remove 90 percent of the naphthalene from the soil is 599, which would require approximately 10 years to attain. For the surfactant solution, the amount of time required is reduced to approximately 4.5 years. This reduction in time would most likely reduce costs of energy as well as free-up equipment for other purposes.

The same analysis can be performed for each flow rate and required level of removal efficiency. The period of time required to attain each level of removal efficiency at all flow rates is reduced by approximately 40 to 60 percent by using a surfactant solution. It is interesting to note that this range is approximately the same as the mass removal efficiencies previously described using the asymptotic values presented in Table 5.13. It is also very interesting to note that this time savings, as well as the mass removal efficiency, compares favorably with the 65 percent reduction in the partition coefficient reported from the equilibrium studies. From this one study it cannot be said that there is a correlation between the reduction in the partition coefficient and the reduction in time required to attain a specified level of contaminant removal, but if subsequent studies produce similar results, the reduction in the partition coefficient may be useful in predicting cost savings by surfactant usage.

Observations on Permeability Effects of Surfactant Usage

The pressures on the inlet sides of the columns were monitored throughout the column runs. One of the criteria for selecting the

surfactant for use in this study was that it have minimal clay particle dispersion effects to ensure that an aquifer's permeability would not be affected. Only one of the surfactants tested showed a lower clay particle dispersion effect than the one used for this study, and that particular surfactant, Tween 20, was a constituent of the mixture used. The influent pressures observed for the experiments conducted with surfactants are shown in Appendix F.

In most cases, the columns used for surfactant elutions showed changes in inlet pressures, whereas those with water elutions remained relatively constant. The nature of these columns was such that when the soil began to compress and the head loss increased, it appeared that these two factors were self perpetuating; i.e., an increase in pressure loss caused compression of the column which caused more pressure loss, etc. This was evident in preliminary column testing with water alone, and could be initiated by pressure surges in the system.

The pressure changes noted throughout the column experiments appeared to be related to the flow rate used for elution. For example, when the pump was set to a flow rate of 20 mL/h, the pressure remained fairly constant with readings between approximately 1.0 to 2.0 psi. At 40 mL/h, the pressure remained constant until approximately 17 pore volumes had passed, and then slowly began to increase. At the conclusion of this particular run, 67.9 pore volumes, the pressure had increased to 5.5 psi. For the 60 mL/h run, the pressure began to build at 62 pore volumes from 2.0 psi to 3.2 psi. Once compression of the soil began, the pressure increased more rapidly and reached 33.0 psi by the end of the run which occurred after 95 pore volumes had been eluted.

The experiment conducted at 90 mL/h showed the most severe pressure changes. The pressure began to rise immediately after initiation

of the elution phase of the experiment. The increase in flow rate from 60 mL/h to 90 mL/h may be partially responsible for this. After four hours had elapsed the pressure increased to 21 psi and slowly increased over the next ten hours to 28 psi. At the conclusion of the experiment, the soil had compressed to approximately 90 percent of its initial depth, and the pressure reached 45 psi.

Although the pressures increased significantly in some cases, it is doubtful that this is entirely attributable to the presence of the surfactant. It is more likely that the surfactant had a relatively small effect, but once compression of the soil began the self-perpetuating feature of the system resulted in excessive pressure increases. It appears, consequently, that the surfactant influenced the permeability. Nonetheless, the effects exclusively attributable to the surfactant cannot be ascertained.

Changes in permeability for an actual application of a surfactant solution in the field would be very undesirable. Obviously, pressure changes to the extent exhibited by the experiment conducted at 90 mL/h with the surfactant solution could not be tolerated. The fact that permeability effects were noted for a surfactant exhibiting one of the smallest clay particle dispersion effects can be significant. More research is needed in this area to determine the possibility of formulating the mixture; i.e. using different relative amounts of each surfactant type, to minimize the clay particle dispersion effect.

CHAPTER VI

SUMMARY AND CONCLUSIONS

An experimental program was conducted to study the effects of surfactants on the sorption of naphthalene on aquifer material. Different types of surfactants were tested for their applicability, and a method was established to select a surfactant that showed the greatest potential for use for a pump and treat groundwater remediation program. Preliminary experiments were conducted to study the rates of naphthalene and surfactant sorption to four types of aquifer material. Subsequent studies investigated the effect of the surfactant solution on the equilibrium desorption of naphthalene from three types of aquifer material, followed by a column study to ascertain surfactant performance in a dynamic system. The results of the experimental program led to the following statements of summary and conclusion.

1. The surfactant characteristics that are important relative to their use in a pump and treat remediation project include solubility, critical micelle concentration, clay dispersion effects, soil sorption, and solubilization of contaminants. Anionic, nonionic and various mixtures of surfactants were tested to determine these characteristics.
2. Some anionic surfactants and mixtures comprised of at least one anionic surfactant formed precipitates when exposed to an aqueous electrolyte solution containing calcium chloride. This did not occur for any of the nonionic or mixtures of nonionic surfactants.
3. Nonionic surfactants exhibited much lower critical micelle concentrations (CMC) than did anionic surfactants. All mixtures of two nonionic surfactants exhibited low CMCs, with the CMC of the mixture closer to that of the constituent with the lowest CMC. For mixtures of nonionic and anionic surfactants, the CMC was approximated by twice the CMC of the nonionic surfactant, indicating that the micelles were formed primarily by the nonionic molecules. The CMCs determined for the mixtures of two anionic surfactants showed no trend; one mixture showed a substantial decrease in CMC, while another increased the CMC.

4. All nonionic surfactants and mixtures of nonionic surfactants showed a tendency to suspend clay particles in a solution with Charleston soil. Nearly all anionic surfactants and mixtures that were comprised of at least one anionic surfactant destabilized colloidal material resulting in decreased solution clay content.
5. Nonionic surfactants, and mixtures thereof, showed the greatest extents of adsorption to the Charleston soil at the surfactant concentration used for this study. Although anionic surfactants showed lesser extents of adsorption, this may have been a consequence of the experimental method. The surfactant concentration used was above the CMC for the nonionic surfactants, but below the CMC for most anionic surfactants. The anionic surfactants may have shown greater extents of adsorption had higher surfactant concentrations been used.
6. In most cases, anionic surfactants solubilized naphthalene from the Charleston soil to a greater extent than did nonionic surfactants. Surfactant mixtures showed no general trends regarding the effectiveness of solubilizing naphthalene. Some mixtures solubilized naphthalene very well, whereas others were not as effective as water alone.
7. The ideal surfactant that might be used in a pump and treat groundwater remediation program should be soluble, exhibit minimal soil sorption, have the same clay particle dispersion characteristics as water, be an excellent solubilization agent for naphthalene, and be nontoxic and biodegradable. An ideal surfactant could not be identified among the surfactants tested.
8. A systematic screening procedure was developed to select the most appropriate surfactant based on criteria established by the most objective means available. Applying this procedure resulted in the selection of a nonionic/anionic surfactant mixture composed of Aerosol AY-65 and Tween 20 for use in the naphthalene desorption studies. .
9. No statistical evidence was detected to indicate that the CMC of the selected surfactant was affected by changes in pH or ionic strength. It's stability in this regard is considered advantageous for applications in a groundwater remediation system.
10. Equilibrium sorption characteristics of the selected surfactant mixture resembled those of a nonionic surfactant for the range of surfactant concentrations used to develop the isotherm. It was concluded that most of the sorption was attributable to the nonionic surfactant.
11. Different rates of approach to the equilibrium sorption capacity were observed for naphthalene adsorption onto the four types of soils studied. The equilibrium capacities of the Greenville and Tinker soils were approached very rapidly,

whereas the equilibrium capacities of the Charleston and California soils were approached much more slowly. The approach to equilibrium was slowest for the Charleston soil requiring over two weeks to attain 95 percent of its equilibrium sorption capacity.

12. The rates of approach to adsorption equilibrium correlated with the amount and types of clays associated with each soil. The rate decreased as the amount of expandable clays, particularly montmorillonite, increased.
13. Much longer equilibration times may be required to approach thermodynamic equilibrium closely in sorption experiments involving hydrophobic organic compounds and soils with expandable clays than have been reportedly used by some researchers.
14. Equilibrium sorption capacities correlated with the amounts and types of clay present. Capacities increased as the clay fraction increased, and greater equilibrium sorption capacities were observed when the clay fraction included montmorillonite.
15. A rapid approach to sorption equilibrium for the selected surfactant with the Charleston soil was observed with the soil being within 99 percent of its equilibrium surfactant sorption capacity by 48 hours.
16. Sorption isotherms developed for naphthalene adsorbing to three soils were linear. The calculated partition coefficients correlated with the equilibrium sorption capacities determined during the kinetic studies. The Charleston soil exhibited the greatest extent of adsorption followed by the California soil, while the least was observed for the Greenville soil.
17. From equilibrium sorption studies, no evidence of irreversible sorption of naphthalene on Greenville and California soils was detected. Statistical evidence, however, did point to a slight extent of irreversible sorption of naphthalene on the Charleston soil at the 50:50 dilution ratio used for this study. Results from the column study, however, indicated a much greater fraction of the adsorbed naphthalene was resistant to release from the soil. This observation most likely resulted from the fact that eluting the soil with naphthalene-free water had the effect of a much larger dilution ratio, making the nonlabile naphthalene fraction much more apparent.
18. The partition coefficient for naphthalene desorption from the Charleston soil initially decreased as surfactant solution concentrations increased, and subsequently decreased at greater surfactant concentrations. This observation was believed to result from adsorption of the anionic surfactant at higher surfactant concentrations leading to the formation of hemimicelles on the soil surface. There was statistical evidence that a most efficient surfactant concentration existed.

19. There was evidence that the partition coefficient for naphthalene on Greenville soil increased as surfactant solution concentration increased. This soil was shown to have a zero point of charge approximately equal to the soil solution pH, and the sorption of the anionic surfactant may have been enhanced by the presence of positive sorption sites on the soil surface. Under these conditions, hemimicelle formation is enhanced with a subsequent removal of naphthalene from solution.
20. Surfactant interactions with soil are important factors when estimating the effects a surfactant solution may have on the mobility of a contaminant.
21. A symmetrical ogive used to model the naphthalene column breakthrough curves represented the data well. This indicated that soil sorption within the column primarily was to external surfaces.
22. Partition coefficients calculated using the inflection point of the breakthrough curve (retardation factor) were consistently lower than the partition coefficient calculated from equilibrium batch tests. This observation most likely resulted from a lack of local equilibrium caused by relatively short retention times for naphthalene in the column.
23. Partition coefficients calculated from the mass adsorbed on the soil in the column compared favorably with the partition coefficient calculated in the batch equilibrium studies.
24. Naphthalene removal efficiency did not appear to be significantly affected by changes in flow rate for either the water or surfactant elutions.
25. Removal efficiencies of naphthalene were greater for surfactant solutions than for water alone at all flow rates. The increase in efficiency compared favorably with the decrease in the partition coefficient determined from batch equilibrium studies.
26. The surfactant was observed to have an effect on the permeability of the soil within the column. Even though the selected surfactant exhibited one of the lowest effects on clay particle dispersion, it was sufficient to decrease the permeability of the soil. More research is required in this area before a surfactant solution could be applied in the field.

CHAPTER VII

ENGINEERING SIGNIFICANCE

The use of a surfactant solution was shown to decrease the number of pore volumes required to be pumped through soil in order to remove a hydrophobic organic contaminant. This observation indicates that surfactant solutions have the potential for increasing the efficiency of contaminant extraction when applied in conjunction with a pump and treat groundwater remediation process, reducing the time required to complete the remediation by up to several years.

Equilibrium sorption studies indicated that one particular surfactant would not be suitable for all situations. In fact, the same surfactant that mobilizes contaminants for one soil type may have the effect of immobilizing the same contaminants when applied to a different soil. Also, only one compound was used for these studies, and it is likely that other surfactants would be more appropriate for different types of contaminants. Although soil and surfactant characterizations can be time consuming and expensive, the interactions among the soils, surfactants and contaminants are of such a complex nature that these characterizations must be conducted in order to design an effective treatment process. The current state of knowledge is not sufficiently developed to allow prediction of these interactions without considerable experimental work.

The surfactant characteristics identified in this report as well as the method used to select an appropriate surfactant proved to be an effective means of making the proper surfactant selection. It is further recommended, however, that more attention be paid to formulating the

surfactant mixture to have minimal effects on the dispersion of clay particles. Tests should be conducted with different relative amounts of the constituent surfactants to determine a ratio resulting in the least effect on clay particles while still maintaining other characteristics essential to the successful solubilization of the contaminants. In this regard, mixtures of anionic and nonionic surfactants would be most appropriate. Nonionic surfactants tend to disperse clay while anionic surfactants destabilize colloidal material. A ratio that results in a neutralization of these two effects would be desirable.

The results of the column studies indicated that the efficiency of mass of contaminant removal, as well as the reduction in time required to affect the remediation for a pump and treat process, could be increased by approximately 40 to 60 percent. However, the feasibility of using such a system will, in the final analysis, be determined on economics considerations. Although an economic analysis is beyond the scope of this report, it is obvious that the costs associated with using a surfactant solution would have to be more than offset by the reduction in energy costs and time required to effect the remediation.

APPENDICES

Appendix A

Additional Tests of Surfactants

Table A-1. Rate of Surfactant Mixture Tween 20/AY-65 Adsorption to Charleston Soil; Data and Calculations

Sample	Time (hr)	Mass Soil (g)	Initial Surfactant Concentration (%)	Surfactant Concentration After Contact (%)	C _s ^a (mg/L)	Mass Adsorbed per gram soil (mg/g)
1	5	5.0054	0.600	0.205	2255	22
2	17	5.0051	0.600	0.173	1903	23
3	29	5.0106	0.600	0.109	1199	27
4	41	5.0125	0.600	0.113	1243	27
5	53	5.0056	0.600	0.131	1441	26
6	65	5.0123	0.600	0.118	1298	26
7	77	5.0048	0.600	0.120	1320	26
8	89	5.0003	0.600	0.129	1419	26
9	101	5.0003	0.600	0.105	1155	27

^abased on specific gravity of surfactant = 1.1.

Table A-2. Equilibrium Sorption Study for Surfactant Mixture Tween 20/AY-65 Adsorption to Charleston Soil; Data and Calculations

Samp	Mass Soil (g)	Initial Surfactant Concentration (%)	Surfactant Concentration After Contact ^a (%)	Average (%)	C _s ^b (mg/L)	Mass Adsorbed per gram soil (mg/g)
2	5.0052	0.010	0.002	0.002	22	0
14	5.0036	0.010	*			
3	5.0023	0.020	0.002	0.002	17	1
15	5.0009	0.020	0.001			
4	5.0010	0.040	0.007	0.007	77	2
16	5.0058	0.040	*			
5	5.0025	0.060	0.009	0.011	121	3
17	5.0031	0.060	0.013			
6	5.0096	0.080	0.013	0.013	143	4
18	5.0013	0.080	*			
7	5.0050	0.100	0.015	0.017	187	5
19	5.0052	0.100	0.019			
8	5.0067	0.200	*	0.025	275	10
20	5.0066	0.200	0.025			
9	5.0028	0.400	0.027	0.028	308	20
46	5.0005	0.400	0.029			
10	5.0005	0.600	0.106	0.114	1254	27
22	5.0014	0.600	0.122			
11	5.0093	0.800	0.290	0.333	3658	26
23	5.0031	0.800	0.375			
12	5.0068	1.000	0.367	0.367	4037	35
24	5.0005	1.000	*			

^alost samples occurred due to leakage while being rotated in tumblers.

^bbased on specific gravity of surfactant = 1.1.

Appendix B

Naphthalene Adsorption Kinetics

Table B-1. Data and Calculations for Determining the Kinetic Response of Naphthalene Adsorbing onto Charleston Soil

Sample	M ₀ (gm)	V ₀ (ml)	V _e (ml)	V _a (ml)	M _{0t} (μgm)	DPM/mL (DPM/mL)	M _a (μgm)	V _a (mL)	M _g (μgm)	Γ (μ/gm)	Time (hrs)
1	1.0026	0.394	5.000	0.200	2.063	31162	2.063	0.576	0.003	0.000	0
6	1.0013	0.394	5.000	0.200	2.063	29447	1.899	0.576	0.003	0.164	1
11	1.0067	0.398	5.000	0.200	2.063	28769	1.855	0.574	0.003	0.207	4
16	1.0051	0.395	5.000	0.200	2.063	28213	1.819	0.575	0.003	0.243	11
21	1.0009	0.393	5.000	0.200	2.063	28030	1.807	0.577	0.003	0.256	22
26	1.0026	0.394	5.000	0.200	2.063	27510	1.774	0.576	0.003	0.289	46
31	1.0030	0.394	5.000	0.200	2.063	24151	1.557	0.576	0.003	0.504	70
36	1.0038	0.394	5.000	0.200	2.063	12490	0.805	0.576	0.001	1.253	100
41	1.0009	0.393	5.000	0.200	2.063	14423	0.930	0.577	0.002	1.132	142
46	1.0069	0.396	5.000	0.200	2.063	7936	0.512	0.574	0.001	1.541	166
51	1.0047	0.395	5.000	0.200	2.063	10724	0.691	0.575	0.001	1.365	190
56	1.0017	0.394	5.000	0.200	2.063	4884	0.314	0.576	0.001	1.748	464
61	1.0045	0.395	5.000	0.200	2.063	5293	0.341	0.575	0.001	1.714	464
66	1.0040	0.395	5.000	0.200	2.063	4873	0.314	0.575	0.001	1.742	464

Table B-2. Data and Calculations for Determining the Kinetic Response of Naphthalene Adsorbing onto California Soil

Sample	M ₀ (gm)	V ₀ (ml)	V _e (ml)	V _a (ml)	M _{0t} (μgm)	DPM/mL (DPM/mL)	M _a (μgm)	V _a (mL)	M _g (μgm)	Γ (μ/gm)	Time (hrs)
2	1.0090	0.457	5.000	0.200	2.063	29796	2.063	0.513	0.003	0.000	0
7	1.0013	0.454	5.000	0.200	2.063	29065	1.874	0.516	0.003	0.189	1
12	1.0043	0.455	5.000	0.200	2.063	28265	1.822	0.515	0.003	0.240	4
17	1.0067	0.456	5.000	0.200	2.063	28188	1.817	0.514	0.003	0.244	11
22	1.0083	0.457	5.000	0.200	2.063	17910	1.155	0.513	0.002	0.901	22
27	1.0078	0.457	5.000	0.200	2.063	17826	1.149	0.513	0.002	0.907	46
32	1.0029	0.454	5.000	0.200	2.063	18459	1.190	0.516	0.002	0.870	70
37	1.0058	0.456	5.000	0.200	2.063	16183	1.043	0.514	0.002	1.014	100
42	1.0054	0.455	5.000	0.200	2.063	17751	1.144	0.515	0.002	0.914	142
47	1.0016	0.454	5.000	0.200	2.063	11111	0.716	0.516	0.001	1.345	166
52	1.0022	0.454	5.000	0.200	2.063	17001	1.096	0.516	0.002	0.965	190
57	1.0050	0.455	5.000	0.200	2.063	11884	0.766	0.515	0.001	1.290	464
62	1.0011	0.453	5.000	0.200	2.063	11178	0.721	0.517	0.001	1.341	464
67	1.0003	0.453	5.000	0.200	2.063	11901	0.767	0.517	0.001	1.295	464

Table B-3. Data and Calculations for Determining the Kinetic Response of Naphthalene Adsorbing onto Greenville Soil

Sample	M ₀ (gm)	V ₀ (ml)	V _s (ml)	V _n (ml)	M _{0c} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _n (mL)	M _g (μgm)	r (μ/gm)	Time (hrs)
1	1.0017	0.491	5.000	0.200	2.063	26363	1.700	0.479	0.002	0.363	7
2	1.0077	0.494	5.000	0.200	2.063	26712	1.722	0.476	0.002	0.338	21
3	1.0050	0.492	5.000	0.200	2.063	27574	1.778	0.478	0.002	0.284	33
4	1.0070	0.493	5.000	0.200	2.063	27122	1.749	0.477	0.002	0.312	45
5	1.0048	0.492	5.000	0.200	2.063	26733	1.724	0.478	0.002	0.338	57
6	1.0056	0.493	5.000	0.200	2.063	26495	1.708	0.477	0.002	0.353	69
7	1.0009	0.490	5.000	0.200	2.063	25030	1.614	0.480	0.002	0.449	81
8	1.0088	0.494	5.000	0.200	2.063	26955	1.738	0.476	0.002	0.322	93
9	1.0011	0.491	5.000	0.200	2.063	25837	1.666	0.479	0.002	0.397	105
10	1.0086	0.494	5.000	0.200	2.063	25725	1.659	0.476	0.002	0.401	117
11	1.0014	0.491	5.000	0.200	2.063	26516	1.710	0.479	0.002	0.353	129
12	1.0056	0.493	5.000	0.200	2.063	25172	1.623	0.477	0.002	0.438	141

Table B.4. Data and Calculations for Determining the Kinetic Response of Naphthalene Adsorbing onto Tinker Soil

Sample	M ₀ (gm)	V ₀ (ml)	V _s (ml)	V _n (ml)	M _{0c} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _n (mL)	M _g (μgm)	r (μ/gm)	Time (hrs)
1	1.0006	0.400	5.000	0.200	1.989	30915	1.993	0.570	0.003	-0.007	0
2	1.0013	0.401	5.000	0.200	1.989	30339	1.956	0.569	0.003	0.030	11
3	1.0012	0.400	5.000	0.200	1.989	28866	1.861	0.570	0.003	0.125	23
4	1.0001	0.400	5.000	0.200	1.989	30428	1.962	0.570	0.003	0.024	35
5	1.0053	0.402	5.000	0.200	1.989	29667	1.913	0.568	0.003	0.073	47
6	1.0034	0.401	5.000	0.200	1.989	29348	1.892	0.569	0.003	0.093	59
7	1.0013	0.401	5.000	0.200	1.989	30213	1.948	0.569	0.003	0.038	71
8	1.0020	0.401	5.000	0.200	1.989	29377	1.894	0.569	0.003	0.092	83
9	1.0030	0.401	5.000	0.200	1.989	29955	1.931	0.569	0.003	0.054	95
10	1.0068	0.403	5.000	0.200	1.989	29055	1.873	0.567	0.003	0.112	107

Appendix C

Naphthalene Desorption Kinetics

Table C-1. Data and Calculations for Determining the Kinetic Response of Naphthalene Desorbing from Charleston Soil

(From Ads. Data)										
Sample	M ₀ (gms)	C ₀ (mg/L)	V ₀ + V _n (mL)	M _{n1} (μgm)	DPM/mL (DPM/mL)	M _n (μgm)	V _n (mL)	M _n (μgm)	M _n /M ₀ (μgm/gm)	Time (hrs)
91	1.0021	0.071	5.200	0.192	5108	0.329	0.578	0.001	0.137	2
92	1.0019	0.070	5.200	0.190	4907	0.318	0.578	0.001	0.128	14
93	1.0030	0.078	5.200	0.205	5778	0.372	0.578	0.001	0.167	26
94	1.0076	0.074	5.200	0.199	5818	0.375	0.574	0.001	0.175	38
95	1.0070	0.075	5.200	0.203	8108	0.394	0.574	0.001	0.189	50
96	1.0005	0.072	5.200	0.195	5989	0.385	0.577	0.001	0.190	62
97	1.0009	0.081	5.200	0.218	8093	0.393	0.577	0.001	0.174	74

Table C-2. Data and Calculations for Determining the Kinetic Response of Naphthalene Desorbing from California Soil

(From Ads. Data)										
Sample	M ₀ (gms)	C ₀ (mg/L)	V ₀ + V _n (mL)	M _{n1} (μgm)	DPM/mL (DPM/mL)	M _n (μgm)	V _n (mL)	M _n (μgm)	M _n /M ₀ (μgm/gm)	Time (hrs)
82	1.0038	0.098	5.200	0.280	8388	0.412	0.515	0.001	0.151	7
83	1.0044	0.109	5.200	0.294	7517	0.485	0.515	0.001	0.190	21
84	1.0048	0.030	5.200	0.244	8481	0.417	0.515	0.001	0.172	33
85	1.0028	0.088	5.200	0.239	8035	0.389	0.518	0.001	0.150	45
86	1.0057	0.109	5.200	0.295	7183	0.483	0.514	0.001	0.167	57
87	1.0090	0.098	5.200	0.259	8631	0.428	0.513	0.001	0.187	69
88	1.0003	0.083	5.200	0.223	8285	0.404	0.517	0.001	0.181	81
93	1.0033	0.078	5.200	0.205	5860	0.378	0.518	0.001	0.173	93
95	1.0018	0.069	5.200	0.187	5401	0.348	0.518	0.001	0.181	117
81	1.0004	0.098	5.200	0.285	8510	0.420	0.517	0.001	0.154	141

Table C-3. Data and Calculations for Determining the Kinetic Response of Naphthalene Desorbing from Greenville Soil

Sample	(From Ads. Data)									Time (hrs)
	M_0 (gms)	C_0 (mg/L)	$V_0 + V_a$ (mL)	$M_{0.1}$ (μ gm)	DPM/mL (DPM/mL)	M_a (μ gm)	V_a (mL)	M_a (μ gm)	M_a/M_0 (μ gm/gm)	
13	1.0078	0.328	5.200	0.394	8611	0.555	0.486	0.001	0.162	5
14	1.0005	0.315	5.200	0.378	9088	0.588	0.490	0.001	0.208	17
15	1.0070	0.324	5.200	0.389	8776	0.566	0.488	0.001	0.176	41
16	1.0042	0.318	5.200	0.381	9325	0.601	0.488	0.001	0.220	53
17	1.0097	0.311	5.200	0.373	9001	0.580	0.485	0.001	0.208	65
18	1.0084	0.319	5.200	0.383	8316	0.536	0.486	0.001	0.154	77
24	1.0033	0.319	5.200	0.383	9277	0.598	0.486	0.001	0.215	99
19	1.0012	0.328	5.200	0.394	8768	0.565	0.489	0.001	0.171	111
20	1.0008	0.330	5.200	0.397	8844	0.570	0.490	0.001	0.173	123
21	1.0012	0.328	5.200	0.394	8861	0.571	0.489	0.001	0.176	124
22	1.0018	0.319	5.200	0.383	9288	0.599	0.489	0.001	0.218	135
23	1.0013	0.324	5.200	0.389	8456	0.545	0.489	0.001	0.154	147

Table C-4. Data and Calculations for Determining the Kinetic Response of Naphthalene Desorbing from Tinker Soil

Sample	(From Ads. Data)									Time (hrs)
	M_0 (gms)	C_0 (mg/L)	$V_0 + V_a$ (mL)	$M_{0.1}$ (μ gm)	DPM/mL (DPM/mL)	M_a (μ gm)	V_a (mL)	M_a (μ gm)	M_a/M_0 (μ gm/gm)	
11	1.0001	0.361	5.200	0.434	****	*****	*****	*****	*****	*
12	1.0052	0.368	5.200	0.441	8752	0.435	0.578	0.001	-0.006	9
13	1.0012	0.360	5.200	0.432	8701	0.432	0.580	0.001	-0.001	21
14	1.0032	0.363	5.200	0.435	6567	0.423	0.579	0.001	-0.012	33
15	1.0018	0.357	5.200	0.428	6993	0.451	0.579	0.001	0.022	45
16	1.0025	0.373	5.200	0.448	6661	0.429	0.579	0.001	-0.019	57
17	1.0072	0.364	5.200	0.437	8725	0.434	0.577	0.001	-0.004	68
18	1.0061	0.359	5.200	0.430	6551	0.422	0.578	0.001	-0.009	80
19	1.0006	0.357	5.200	0.429	****	*****	*****	*****	*****	**
20	1.0033	0.365	5.200	0.438	6666	0.430	0.579	0.001	-0.009	92

Appendix D

Adsorption Isotherms

Table D-1. Calculations of Mass Naphthalene Injected into Each Sample, and Mass Naphthalene Contained in the Blanks After Equilibration for Charleston Soil Sorption Studies

Vol Water (mL)	Vol Nap. Solution (mL)	Initial DPM/mL	Avg Initial DPM/mL	Blank DPM/mL	Blank Avg DPM/mL	Blank Concentration Naph ($\mu\text{gm/L}$)	Blank Mass Naph (μgm)
5.00	0.050	8979	8972	8282	8267	102	.518
5.00		8965		8252			
5.00	0.125	20803	20672	19019	18325	227	1.164
5.00		20541		17630			
5.00	0.200	31614	31764	30058	30058	373	1.938
5.00		31914		30058			
5.00	0.275	42946	42921	38835	38994	483	2.550
5.00		42896		39153			
5.00	0.350	52635	52036	44775	45790	568	3.037
5.00		51436		46805			

Table D-2. Data and Calculations for Determining Adsorption Isotherm for Naphthalene and Charleston Soil

Sample	M _s (gm)	V _s (mL)	V ₀ (mL)	V _a (mL)	M ₀ (μgm)	DPM/mL (DPM/mL)	M _a (μgm)	V _a (mL)	M _g (μgm)	Γ (μgm/gm)	C ₀ (mg/L)
1	1.0063	0.395	5.000	0.050	0.518	1462	0.092	0.735	0.000	0.426	0.018
2	1.0030	0.394	5.000	0.050	0.518	1704	0.107	0.736	0.000	0.411	0.021
3	1.0054	0.395	5.000	0.125	1.164	3863	0.245	0.660	0.000	0.918	0.048
4	1.0015	0.394	5.000	0.125	1.164	3830	0.243	0.661	0.000	0.921	0.047
5	1.0016	0.394	5.000	0.200	1.938	5923	0.382	0.586	0.001	1.555	0.073
6	1.0014	0.394	5.000	0.200	1.938	6024	0.388	0.586	0.001	1.549	0.075
7	1.0003	0.393	5.000	0.275	2.550	8107	0.530	0.512	0.001	2.019	0.101
8	1.0039	0.395	5.000	0.275	2.550	7668	0.502	0.510	0.001	2.048	0.095
9	1.0033	0.394	5.000	0.350	3.037	10136	0.672	0.436	0.001	2.364	0.126
10	1.0043	0.395	5.000	0.350	3.037	9873	0.655	0.435	0.001	2.382	0.122
11	1.0078	0.396	5.000	0.050	0.518	1622	0.102	0.734	0.000	0.416	0.020
12	1.0071	0.396	5.000	0.050	0.518	1698	0.106	0.734	0.000	0.411	0.021
13	1.0008	0.393	5.000	0.125	1.164	*	0.000	0.662	0.000	*	*
14	1.0009	0.393	5.000	0.125	1.164	3993	0.254	0.662	0.000	0.910	0.050
15	1.0011	0.393	5.000	0.200	1.938	6065	0.391	0.587	0.001	1.546	0.075
16	1.0040	0.395	5.000	0.200	1.938	6072	0.391	0.585	0.001	1.546	0.075
17	1.0052	0.395	5.000	0.275	2.550	8010	0.524	0.510	0.001	2.026	0.099
18	1.0015	0.394	5.000	0.275	2.550	8542	0.559	0.511	0.001	1.991	0.106
19	1.0003	0.393	5.000	0.350	3.037	10279	0.682	0.437	0.001	2.355	0.127
20	1.0076	0.396	5.000	0.350	3.037	9635	0.639	0.434	0.001	2.397	0.119
21	1.0038	0.394	5.000	0.050	0.518	1851	0.116	0.736	0.000	0.401	0.023
22	1.0031	0.394	5.000	0.050	0.518	1833	0.115	0.736	0.000	0.403	0.023
23	1.0010	0.393	5.000	0.125	1.164	4048	0.257	0.662	0.000	0.907	0.050
24	1.0045	0.395	5.000	0.125	1.164	4203	0.267	0.660	0.001	0.897	0.052
25	1.0030	0.394	5.000	0.200	1.938	6453	0.416	0.586	0.001	0.521	0.080

Table D-2 (continued). Data and Calculations for Determining Adsorption Isotherm for Naphthalene and Charleston Soil

Sample	M ₀ (gm)	V ₀ (mL)	V _s (mL)	V _a (mL)	M _{at} (µgm)	DPH/mL (DPH/mL)	M _a (µgm)	V _a (mL)	M _g (µgm)	r (µgm/gm)	C ₀ (mg/L)
26	1.0017	0.394	5.000	0.200	1.938	8485	0.418	0.588	0.001	1.519	0.080
27	1.0005	0.393	5.000	0.275	2.550	*	0.000	0.512	0.000	*	*
28	1.0043	0.395	5.000	0.275	2.550	8233	0.538	0.510	0.001	2.011	0.102
29	1.0048	0.395	5.000	0.350	3.037	9868	0.655	0.435	0.001	2.382	0.127
30	1.0044	0.395	5.000	0.350	3.037	9171	0.608	0.435	0.001	2.428	0.114
31	1.0007	0.393	5.000	0.050	0.518	1867	0.117	0.737	0.000	0.400	0.023
32	1.0088	0.396	5.000	0.050	0.518	1811	0.113	0.734	0.000	0.404	0.022
33	1.0037	0.394	5.000	0.125	1.164	4081	0.258	0.661	0.000	0.906	0.050
34	1.0020	0.394	5.000	0.125	1.164	4312	0.274	0.661	0.001	0.890	0.053
35	1.0040	0.395	5.000	0.200	1.938	6525	0.421	0.585	0.001	1.517	0.081
36	1.0007	0.393	5.000	0.200	1.938	6364	0.410	0.587	0.001	1.527	0.079
37	1.0075	0.396	5.000	0.275	2.550	8660	0.568	0.509	0.001	1.983	0.107
38	1.0083	0.396	5.000	0.275	2.550	8951	0.585	0.509	0.001	1.964	0.111
39	1.0009	0.393	5.000	0.350	3.037	9823	0.652	0.437	0.001	2.385	0.122
40	1.0006	0.393	5.000	0.350	3.037	10301	0.683	0.437	0.001	2.353	0.128
41	1.0035	0.394	5.000	0.050	0.518	1733	0.109	0.736	0.000	0.409	0.021
42	1.0017	0.394	5.000	0.050	0.518	1665	0.104	0.736	0.000	0.413	0.021
43	1.0079	0.396	5.000	0.125	1.164	3987	0.253	0.659	0.000	0.911	0.049
44	1.0049	0.395	5.000	0.125	1.164	3648	0.232	0.660	0.000	0.932	0.045
45	1.0093	0.397	5.000	0.200	1.938	6133	0.395	0.583	0.001	1.542	0.076
46	1.0068	0.396	5.000	0.200	1.938	6066	0.391	0.584	0.001	1.546	0.075
47	1.0082	0.396	5.000	0.275	2.550	8004	0.523	0.509	0.001	2.026	0.099
48	1.0038	0.394	5.000	0.275	2.550	8224	0.538	0.511	0.001	2.012	0.102
49	1.0017	0.394	5.000	0.350	3.037	9725	0.645	0.438	0.001	2.391	0.121
50	1.0019	0.394	5.000	0.350	3.037	10345	0.686	0.438	0.001	2.350	0.128

* vial cracked during centrifugation

Table D-3. Calculations of Mass Naphthalene Injected into Each Sample, and Mass Naphthalene Contained in the Blanks After Equilibration for California Soil Sorption Studies

Vol Water (mL)	Vol Nap. Solution (mL)	Initial DPM/mL	Avg Initial DPM/mL	Blank DPM/mL	Blank Avg DPM/mL	Blank Concentration Naph ($\mu\text{gm/L}$)	Blank Mass Naph (μgm)
5.00	0.050	9016	9000	8511	8685	108	0.544
5.00		8983		8858			
5.00	0.125	20700	20572	19423	19875	246	1.263
5.00		20443		20326			
5.00	0.200	31469	31389	30716	30944	384	1.995
5.00		31308		31172			
5.00	0.275	(BAD)	42474	40689	40476	502	2.647
5.00		42474		40263			
5.00	0.350	48045	50182	50422	50466	626	3.347
5.00		52318		50510			

Table D-4. Data and Calculations for Determining Adsorption Isotherm for Naphthalene and California Soil

Sample	M_a (gm)	V_a (mL)	V_o (mL)	V_n (mL)	M_{at} (μ gm)	DPM/mL (DPM/mL)	M_a (μ gm)	V_a (mL)	M_g (μ gm)	Γ (μ gm/gm)	C_o (mg/L)
1	1.0003	0.450	5.000	0.050	0.544	1502	0.094	0.680	0.000	0.449	0.019
2	1.0003	0.450	5.000	0.050	0.544	5126	0.321	0.680	0.001	0.222	0.064
3	1.0051	0.452	5.000	0.125	1.263	8179	0.393	0.603	0.001	0.885	0.077
4	1.0038	0.452	5.000	0.125	1.263	5949	0.378	0.603	0.001	0.881	0.074
5	1.0069	0.453	5.000	0.200	1.995	10985	0.707	0.527	0.001	1.278	0.136
6	1.0004	0.450	5.000	0.200	1.995	9824	0.633	0.530	0.001	1.360	0.122
7	1.0029	0.451	5.000	0.275	2.647	9614	0.629	0.454	0.001	2.012	0.119
8	1.0028	0.451	5.000	0.275	2.647	12555	0.821	0.454	0.001	1.820	0.156
9	1.0040	0.452	5.000	0.350	3.347	16576	1.100	0.378	0.001	2.238	0.206
10	1.0029	0.451	5.000	0.350	3.347	18363	1.218	0.379	0.001	2.122	0.228
11	1.0025	0.451	5.000	0.050	0.544	5105	0.320	0.679	0.001	0.223	0.063
12	1.0074	0.453	5.000	0.050	0.544	2851	0.179	0.677	0.000	0.362	0.035
13	1.0077	0.453	5.000	0.125	1.263	10966	0.697	0.602	0.001	0.561	0.136
14	1.0091	0.454	5.000	0.125	1.263	10423	0.662	0.601	0.001	0.594	0.129
15	1.0034	0.452	5.000	0.200	1.995	12076	0.779	0.528	0.001	1.211	0.150
16	1.0054	0.452	5.000	0.200	1.995	8828	0.569	0.528	0.001	1.417	0.109
17	1.0003	0.450	5.000	0.275	2.647	13401	0.876	0.455	0.001	1.769	0.186
18	1.0028	0.451	5.000	0.275	2.647	26620	1.741	0.454	0.002	0.901	0.330
19	1.0025	0.451	5.000	0.350	3.347	13445	0.892	0.379	0.001	2.449	0.167
20	1.0022	0.451	5.000	0.350	3.347	12387	0.822	0.379	0.001	2.519	0.154
21	1.0040	0.452	5.000	0.050	0.544	5012	0.314	0.678	0.001	0.228	0.062
22	1.0008	0.450	5.000	0.050	0.544	1883	0.118	0.680	0.000	0.425	0.023
23	1.0039	0.452	5.000	0.125	1.263	5959	0.379	0.603	0.001	0.880	0.074
24	1.0070	0.455	5.000	0.125	1.263	3545	0.225	0.602	0.000	1.030	0.044
25	1.0054	0.452	5.000	0.200	1.995	9196	0.593	0.528	0.001	1.394	0.114

Table D-4 (continued) . Data and Calculations for Determining Adsorption Isotherm for Naphthalene and California Soil

Sample	M _a (gm)	V _s (mL)	V ₀ (mL)	V _a (mL)	M _{at} (μgm)	DPH/mL (DPH/mL)	M ₀ (μgm)	V _a (mL)	M _g (μgm)	Γ (μgm/gm)	C _a (mg/L)
26	1.0077	0.453	5.000	0.200	1.995	14634	0.943	0.527	0.001	1.042	0.181
27	1.0012	0.451	5.000	0.275	2.647	11885	0.777	0.454	0.001	1.867	0.147
28	1.0009	0.450	5.000	0.275	2.647	14684	0.960	0.455	0.001	1.684	0.182
29	1.0039	0.452	5.000	0.350	3.347	14098	0.935	0.378	0.001	2.402	0.175
30	1.0032	0.451	5.000	0.350	3.347	10719	0.711	0.379	0.001	2.627	0.133
31	1.0026	0.451	5.000	0.050	0.544	2408	0.151	0.679	0.000	0.392	0.030
32	1.0044	0.452	5.000	0.050	0.544	1601	0.100	0.678	0.000	0.441	0.020
33	1.0031	0.451	5.000	0.125	1.263	5383	0.342	0.604	0.001	0.917	0.067
34	1.0033	0.451	5.000	0.125	1.263	7325	0.465	0.604	0.001	0.794	0.091
35	1.0001	0.450	5.000	0.200	1.995	9170	0.591	0.530	0.001	1.403	0.114
36	1.0002	0.450	5.000	0.200	1.995	7866	0.507	0.530	0.001	1.487	0.098
37	1.0002	0.450	5.000	0.275	2.647	27106	1.773	0.455	0.002	0.872	0.336
38	1.0010	0.450	5.000	0.275	2.647	11381	0.744	0.455	0.001	1.900	0.141
39	1.0014	0.451	5.000	0.350	3.347	10246	0.680	0.379	0.001	2.663	0.127
40	1.0034	0.452	5.000	0.350	3.347	16833	1.117	0.378	0.001	2.222	0.209
41	1.0033	0.451	5.000	0.050	0.544	2341	0.147	0.679	0.000	0.396	0.029
42	1.0009	0.450	5.000	0.050	0.544	2337	0.146	0.680	0.000	0.397	0.029
43	1.0091	0.454	5.000	0.125	1.263	5236	0.333	0.601	0.001	0.921	0.065
44	1.0028	0.451	5.000	0.125	1.263	12527	0.796	0.604	0.001	0.464	0.155
45	1.0009	0.450	5.000	0.200	1.995	6371	0.411	0.530	0.001	1.582	0.079
46	1.0044	0.452	5.000	0.200	1.995	9178	0.592	0.528	0.001	1.396	0.114
47	1.0012	0.451	5.000	0.275	2.647	14743	0.964	0.454	0.001	1.680	0.183
48	1.0018	0.451	5.000	0.275	2.647	22498	1.471	0.454	0.002	1.172	0.279
49	1.0045	0.452	5.000	0.350	3.347	13626	0.904	0.378	0.001	2.432	0.169
50	1.0078	0.454	5.000	0.350	3.347	25991	1.724	0.376	0.002	1.609	0.322

Table D-5. Calculations of Mass Naphthalene Injected into Each Sample, and Mass Naphthalene Contained in the Blanks After Equilibration for Greenville Soil Sorption Studies

Vol Water (mL)	Vol Nap. Solution (mL)	Initial DPM/mL	Avg Initial DPM/mL	Blank DPM/mL	Blank Avg DPM/mL	Blank Concentration Naph ($\mu\text{gm/L}$)	Blank Mass Naph (μgm)
5.00	0.050	9130	9097	8659	8586	106	0.538
5.00		9063		8513			
5.00	0.125	20492	20492	19795	19964	248	1.269
5.00		(BAD)		20132			
5.00	0.200	31670	31765	30872	30968	384	1.997
5.00		31859		31064			
5.00	0.275	42764	42441	40239	40191	498	2.629
5.00		42117		40143			
5.00	0.350	53193	52904	50877	50968	632	3.381
5.00		52614		51059			

Table D-6. Data and Calculations for Determining Adsorption Isotherm for Naphthalene and Greenville Soil

Sample	M ₀ (gm)	V ₀ (mL)	V _s (mL)	V _a (mL)	M _{at} (µgm)	DPM/mL (DPM/mL)	M ₀ (µgm)	V _a (mL)	M ₀ (µgm)	Γ (µgm/gm)	C ₀ (mg/L)
1	1.0031	0.492	5.000	0.050	0.538	6191	0.388	0.638	0.001	0.149	0.077
2	1.0008	0.490	5.000	0.050	0.538	7150	0.448	0.640	0.001	0.089	0.089
3	1.0052	0.493	5.000	0.125	1.269	16788	1.067	0.562	0.002	0.199	0.208
4	1.0013	0.491	5.000	0.125	1.269	16727	1.063	0.564	0.002	0.204	0.207
5	1.0043	0.492	5.000	0.200	1.997	25595	1.850	0.488	0.002	0.343	0.317
6	1.0009	0.490	5.000	0.200	1.997	26320	1.697	0.490	0.002	0.297	0.326
7	1.0042	0.492	5.000	0.275	2.629	34751	2.273	0.413	0.003	0.352	0.431
8	1.0024	0.491	5.000	0.275	2.629	35020	2.290	0.414	0.003	0.335	0.434
9	1.0088	0.494	5.000	0.350	3.381	42715	2.833	0.336	0.003	0.540	0.530
10	1.0027	0.491	5.000	0.350	3.381	44861	2.976	0.339	0.003	0.401	0.556
11	1.0070	0.493	5.000	0.050	0.538	7462	0.467	0.637	0.001	0.069	0.093
12	1.0035	0.492	5.000	0.050	0.538	7259	0.455	0.638	0.001	0.082	0.090
13	1.0012	0.491	5.000	0.125	1.269	17155	1.090	0.564	0.002	0.176	0.213
14	1.0043	0.492	5.000	0.125	1.269	16484	1.047	0.563	0.002	0.218	0.204
15	1.0095	0.495	5.000	0.200	1.997	25856	1.667	0.485	0.002	0.324	0.321
16	1.0033	0.492	5.000	0.200	1.997	25753	1.660	0.488	0.002	0.333	0.319
17	1.0030	0.491	5.000	0.275	2.629	34883	2.281	0.414	0.003	0.343	0.432
18	1.0046	0.492	5.000	0.275	2.629	34125	2.232	0.413	0.003	0.392	0.423
19	1.0025	0.491	5.000	0.350	3.381	42684	2.831	0.339	0.003	0.545	0.529
20	1.0027	0.491	5.000	0.350	3.381	43450	2.882	0.339	0.003	0.495	0.539
21	1.0013	0.491	5.000	0.050	0.538	7545	0.472	0.639	0.001	0.064	0.094
22	1.0094	0.495	5.000	0.050	0.538	7176	0.449	0.635	0.001	0.087	0.089
23	1.0017	0.491	5.000	0.125	1.269	16637	1.057	0.564	0.002	0.209	0.206
24	1.0071	0.493	5.000	0.125	1.269	16646	1.058	0.562	0.002	0.208	0.206
25	1.0074	0.494	5.000	0.200	1.997	26580	1.714	0.486	0.002	0.278	0.330

Table D-6 (continued). Data and Calculations for Determining Adsorption Isotherm for Naphthalene and Greenville Soil

Sample	M _s (gm)	V _s (mL)	V ₀ (mL)	V _a (mL)	M _{at} (μgm)	DPH/mL (DPH/mL)	M _a (μgm)	V _a (mL)	M _g (μgm)	Γ (μgm/gm)	C _e (mg/L)
26	1.0067	0.493	5.000	0.200	1.997	28185	1.688	0.487	0.002	0.304	0.325
27	1.0032	0.492	5.000	0.275	2.629	34256	2.240	0.413	0.003	0.384	0.425
28	1.0033	0.492	5.000	0.275	2.629	35082	2.294	0.413	0.003	0.330	0.435
29	1.0010	0.490	5.000	0.350	3.381	43568	2.890	0.340	0.003	0.488	0.540
30	1.0083	0.494	5.000	0.350	3.381	43670	2.897	0.338	0.003	0.477	0.541
31	1.0059	0.493	5.000	0.050	0.538	7254	0.454	0.637	0.001	0.082	0.090
32	1.0081	0.494	5.000	0.050	0.538	7146	0.447	0.636	0.001	0.089	0.089
33	1.0051	0.492	5.000	0.125	1.269	16053	1.020	0.563	0.002	0.246	0.199
34	1.0042	0.492	5.000	0.125	1.269	17137	1.089	0.563	0.002	0.177	0.212
35	1.0069	0.493	5.000	0.200	1.997	25184	1.624	0.487	0.002	0.368	0.312
36	1.0015	0.491	5.000	0.200	1.997	28119	1.684	0.489	0.002	0.310	0.324
37	1.0068	0.493	5.000	0.275	2.629	35056	2.293	0.412	0.003	0.331	0.435
38	1.0054	0.493	5.000	0.275	2.629	34479	2.255	0.412	0.003	0.369	0.427
39	1.0064	0.493	5.000	0.350	3.381	44317	2.940	0.337	0.003	0.438	0.549
40	1.0072	0.494	5.000	0.350	3.381	43172	2.864	0.336	0.003	0.511	0.535
41	1.0014	0.491	5.000	0.050	0.538	7507	0.470	0.639	0.001	0.067	0.093
42	1.0006	0.490	5.000	0.050	0.538	4329	0.271	0.640	0.001	0.266	0.054
43	1.0060	0.493	5.000	0.125	1.269	16713	1.062	0.562	0.002	0.204	0.207
44	1.0088	0.494	5.000	0.125	1.269	16606	1.055	0.561	0.002	0.210	0.206
45	1.0017	0.491	5.000	0.200	1.997	25602	1.651	0.489	0.002	0.343	0.317
46	1.0064	0.493	5.000	0.200	1.997	26274	1.694	0.487	0.002	0.298	0.326
47	1.0012	0.491	5.000	0.275	2.629	34331	2.245	0.414	0.003	0.380	0.426
48	1.0056	0.493	5.000	0.275	2.629	34670	2.267	0.412	0.003	0.356	0.430
49	1.0041	0.492	5.000	0.350	3.381	42234	2.801	0.338	0.003	0.574	0.524
50	1.0018	0.491	5.000	0.350	3.381	43292	2.872	0.339	0.003	0.506	0.537

Table D-7. Adsorption Isotherm Data Points and Statistics for Naphthalene and All Soils

Vol. Naph. Stock Soln. (mL)	Mean C _e (mg/L)	Variance	95% Interval Estimate (mg/L)	Mean Γ (μg/g)	Variance	95% Interval Estimate (μg/g)
Charleston						
0.050	0.0213	0.00000248	0.0202 - 0.0224	0.4094	0.0000629	0.4037 - 0.4151
0.125	0.04933	0.00000600	0.0475 - 0.0512	0.9102	0.0001579	0.9006 - 0.9119
0.200	0.0769	0.00000788	0.0749 - 0.0789	1.536A	0.0002017	1.5266 - 1.5470
0.275	0.0124	0.00002353	0.0987 - 0.1062	2.0089	0.0006546	1.9892 - 2.0286
0.350	0.1229	0.00001988	0.1197 - 0.1261	2.3787	0.0058223	2.3614 - 2.3959
California						
0.050	0.0374	0.00033538	0.0243 - 0.0505	0.3535	0.0085794	0.2872 - 0.4198
0.125	0.0912	0.00131107	0.0653 - 0.1171	0.7909	0.0344489	0.6579 - 0.9235
0.200	0.1208	0.00086062	0.0998 - 0.1418	1.3570	0.0225468	1.2500 - 1.4644
0.275	0.2039	0.00644899	0.1465 - 0.2813	1.5677	0.1791984	1.2649 - 1.8705
0.350	0.1900	0.00354822	0.1474 - 0.2326	2.3283	0.0941969	2.1088 - 2.5478
Greenville						
0.050	0.0858	0.00014729	0.0771 - 0.0945	0.1044	0.0037964	0.0603 - 0.1485
0.125	0.2068	0.00001529	0.2040 - 0.2096	0.2051	0.0003958	0.1909 - 0.2193
0.200	0.3217	0.00002979	0.3178 - 0.3256	0.3198	0.0007422	0.3003 - 0.3393
0.275	0.4298	0.00001884	0.4267 - 0.4329	0.3572	0.0005264	0.3408 - 0.3737
0.350	0.5380	0.00009000	0.5312 - 0.5448	0.4973	0.0026422	0.4605 - 0.5341

Appendix E

Equilibrium Desorption Studies

This Appendix contains the data and calculations made to determine desorption isotherms of naphthalene and three soils.

Table E-1. Data and Calculations for Determining Desorption Isotherms for Naphthalene and Charleston Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)												
Sample	M _s (g)	Γ (μg/gm)	C _e (mg/L)	V _s + V _n (mL)	M _{n1} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _A (mL)	M _A (μgm)	M _d (μ/gm)	Γ (μgm/gm)	C _e (mg/L)
No Surfactant added												
1	1.0063	0.426	0.018	5.050	0.046	1161	0.073	0.735	0.000	0.026	0.400	0.014
2	1.0030	0.411	0.021	5.050	0.054	1433	0.090	0.736	0.000	0.036	0.375	0.018
3	1.0054	0.918	0.048	5.125	0.126	3195	0.203	0.660	0.000	0.075	0.842	0.040
4	1.0015	0.921	0.047	5.125	0.125	3301	0.210	0.661	0.000	0.085	0.836	0.041
5	1.0016	1.555	0.073	5.200	0.196	5038	0.325	0.586	0.001	0.126	1.430	0.062
6	1.0014	1.549	0.075	5.200	0.202	5253	0.339	0.586	0.001	0.136	1.413	0.065
7	1.0003	2.019	0.101	5.275	0.279	6958	0.455	0.512	0.001	0.175	1.844	0.086
8	1.0039	2.048	0.095	5.275	0.264	6939	0.454	0.510	0.001	0.189	1.859	0.086
9	1.0033	2.364	0.126	5.350	0.358	8799	0.584	0.436	0.001	0.224	2.140	0.109
10	1.0043	2.382	0.122	5.350	0.349	8808	0.584	0.435	0.001	0.234	2.148	0.109
0.01% Surfactant added												
11	1.0078	0.416	0.020	5.050	0.051	1472	0.092	0.734	0.000	0.040	0.375	0.018
12	1.0071	0.411	0.021	5.050	0.054	1568	0.098	0.734	0.000	0.044	0.367	0.019
13	*	*	*	*	*	*	*	*	*	*	*	*
14	1.0009	0.910	0.050	5.125	0.130	3690	0.234	0.662	0.000	0.104	0.806	0.046
15	1.0011	1.546	0.075	5.200	0.203	5453	0.352	0.587	0.001	0.148	1.398	0.068
16	1.0040	1.546	0.075	5.200	0.203	5843	0.377	0.585	0.001	0.172	1.374	0.072
17	1.0052	2.026	0.099	5.275	0.276	7887	0.516	0.510	0.001	0.238	1.787	0.098
18	1.0015	1.991	0.106	5.275	0.294	8125	0.531	0.511	0.001	0.236	1.754	0.101
19	1.0003	2.355	0.127	5.350	0.363	9902	0.657	0.437	0.001	0.293	2.062	0.123
20	1.0076	2.397	0.119	5.350	0.340	9951	0.660	0.434	0.001	0.316	2.081	0.123

Table E-1 (continued). Data and Calculations for Determining Desorption Isotherms for Naphthalene and Charleston Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)										
Sample	M_s (gm)	Γ ($\mu\text{gm/gm}$)	C_s (mg/L)	$V_s + V_n$ (mL)	$M_{n,i}$ (μgm)	DPH/mL (DPH/mL)	M_n (μgm)	V_n (mL)	M_n (μgm)	C_s (mg/L)
<u>0.05% Surfactant added</u>										
21	1.0038	0.401	0.023	5.050	0.059	2167	0.136	0.736	0.000	0.027
22	1.0031	0.403	0.023	5.050	0.058	2263	0.142	0.736	0.000	0.028
23	1.0010	0.907	0.050	5.125	0.132	4496	0.286	0.662	0.001	0.056
24	1.0045	0.897	0.052	5.125	0.137	5062	0.322	0.660	0.001	0.063
25	1.0030	1.521	0.080	5.200	0.216	7661	0.494	0.586	0.001	0.095
26	1.0017	1.519	0.080	5.200	0.217	7206	0.465	0.586	0.001	0.089
27										
28	1.0043	2.011	0.102	5.275	0.283	9952	0.651	0.510	0.001	0.123
29	1.0048	2.382	0.122	5.350	0.349	12687	0.842	0.435	0.001	0.157
30	1.0044	2.428	0.114	5.350	0.324	11602	0.770	0.435	0.001	0.144
<u>0.25% Surfactant added</u>										
31	1.0007	0.400	0.023	5.050	0.059	2843	0.178	0.737	0.000	0.035
32	1.0088	0.404	0.022	5.050	0.057	2671	0.167	0.734	0.000	0.033
33	1.0037	0.906	0.050	5.125	0.132	6595	0.419	0.661	0.001	0.082
34	1.0020	0.890	0.053	5.125	0.140	6344	0.403	0.661	0.001	0.079
35	1.0040	1.517	0.081	5.200	0.218	11663	0.752	0.585	0.001	0.145
36	1.0007	1.527	0.079	5.200	0.213	11281	0.727	0.587	0.001	0.140
37	1.0075	1.983	0.107	5.275	0.298	15776	1.032	0.509	0.001	0.196
38	1.0083	1.964	0.111	5.275	0.308	14765	0.966	0.509	0.001	0.183
39	1.0009	2.385	0.122	5.350	0.347	18971	1.258	0.437	0.002	0.235
40	1.0006	2.353	0.128	5.350	0.364	17674	1.172	0.437	0.001	0.219

Table E-2. Data and Calculations for Determining Desorption Isotherms for Naphthalene and California Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)													Γ ($\mu\text{gm}/\text{gm}$)	$V_a + V_n$ (mL)	$M_{a,i}$ (μgm)	DPH/mL (DPH/mL)	M_h (μgm)	V_a (mL)	M_a (μgm)	M_d (μgm)	Γ ($\mu\text{gm}/\text{gm}$)	C_e (mg/L)
Sample	M_s (gm)	Γ ($\mu\text{gm}/\text{gm}$)	C_e (mg/L)	$V_a + V_n$ (mL)	$M_{a,i}$ (μgm)	DPH/mL (DPH/mL)	M_h (μgm)	V_a (mL)	M_a (μgm)	M_d (μgm)	Γ ($\mu\text{gm}/\text{gm}$)	C_e (mg/L)										
No Surfactant added																						
1	1.0003	0.449	0.019	5.050	0.047	1393	0.087	0.680	0.000	0.040	0.410	0.017										
2	1.0003	0.222	0.064	5.050	0.162	3546	0.222	0.680	0.000	0.059	0.163	0.044										
3	1.0051	0.865	0.077	5.125	0.201	5093	0.324	0.603	0.001	0.121	0.744	0.063										
4	1.0038	0.881	0.074	5.125	0.194	4998	0.318	0.603	0.001	0.123	0.758	0.062										
5	1.0069	1.276	0.136	5.200	0.367	8587	0.554	0.527	0.001	0.184	1.094	0.106										
6	1.0004	1.360	0.122	5.200	0.329	7890	0.509	0.530	0.001	0.179	1.181	0.098										
7	1.0029	2.012	0.119	5.275	0.331	8471	0.554	0.454	0.001	0.222	1.790	0.105										
8	1.0026	1.820	0.156	5.275	0.432	10324	0.675	0.454	0.001	0.242	1.578	0.128										
9	1.0040	2.238	0.206	5.350	0.586	22157	1.470	0.378	0.002	0.879	1.359	0.275										
10	1.0029	2.122	0.228	5.350	0.649	14721	0.976	0.379	0.001	0.326	1.796	0.183										
0.01% Surfactant added																						
11	1.0025	0.223	0.063	5.050	0.161	3250	0.203	0.679	0.000	0.042	0.181	0.040										
12	1.0074	0.362	0.035	5.050	0.090	2236	0.140	0.677	0.000	0.049	0.313	0.028										
13	1.0077	0.561	0.136	5.125	0.357	6870	0.437	0.602	0.001	0.085		0.561										
14	1.0091	0.594	0.129	5.125	0.339	6593	0.419	0.601	0.001	0.078	0.516	0.082										
15	1.0034	1.211	0.150	5.200	0.404	9193	0.593	0.528	0.001	0.187	1.024	0.114										
16	1.0054	1.417	0.109	5.200	0.296	7155	0.461	0.528	0.001	0.164	1.253	0.089										
17	1.0003	1.769	0.166	5.275	0.461	11119	0.727	0.455	0.001	0.265	1.504	0.138										
18	1.0028	0.901	0.330	5.275	0.916	1623	1.062	0.454	0.001	0.144	0.757	0.201										
19	1.0025	2.449	0.167	5.350	0.475	12189	0.809	0.379	0.001	0.332	2.117	0.151										
20	1.0022	2.519	0.154	5.350	0.438	10875	0.721	0.379	0.001	0.282	2.237	0.135										

Table E-2 (continued). Data and Calculations for Determining Desorption Isotherms for Naphthalene and California Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)												
Sample	M _s (gm)	Γ (μgm/gm)	C _s (mg/L)	V _s + V _n (mL)	M _{n,i} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _n (mL)	M _n (μgm)	M _d (μ/gm)	Γ (μgm/gm)	C _s (mg/L)
0.05% Surfactant added												
21	1.0040	0.228	0.062	5.050	0.158	2647	0.166	0.678	0.000	0.007	0.221	0.033
22	1.0008	0.425	0.023	5.050	0.060	1830	0.115	0.680	0.000	0.055	0.371	0.023
23	1.0039	0.880	0.074	5.125	0.194	4900	0.311	0.603	0.001	0.116	0.764	0.061
24	1.0070	1.030	0.044	5.125	0.115	3471	0.221	0.602	0.000	0.104	0.926	0.043
25	1.0054	1.394	0.114	5.200	0.308	7762	0.500	0.528	0.001	0.191	1.203	0.096
26	1.0077	1.042	0.181	5.200	0.490	9871	0.636	0.527	0.001	0.144	0.898	0.122
27	1.0012	1.867	0.147	5.275	0.409	9596	0.628	0.454	0.001	0.218	1.649	0.119
28	1.0009	1.684	0.182	5.275	0.505	10631	0.695	0.455	0.001	0.189	1.495	0.132
29	1.0039	2.402	0.175	5.350	0.498	12280	0.815	0.378	0.001	0.314	2.088	0.152
30	1.0032	2.627	0.133	5.350	0.379	10543	0.699	0.379	0.001	0.319	2.309	0.131
0.25% Surfactant added												
31	1.0026	0.392	0.030	5.050	0.076	2057	0.129	0.679	0.000	0.052	0.339	0.026
32	1.0044	0.441	0.020	5.050	0.051	1889	0.118	0.678	0.000	0.067	0.374	0.023
33	1.0031	0.917	0.067	5.125	0.175	4797	0.305	0.604	0.001	0.129	0.789	0.059
34	1.0033	0.794	0.091	5.125	0.238	4966	0.316	0.604	0.001	0.076	0.718	0.062
35	1.0001	1.403	0.114	5.200	0.307	7689	0.496	0.530	0.001	0.188	1.215	0.095
36	1.0002	1.487	0.098	5.200	0.263	7765	0.501	0.530	0.001	0.236	1.250	0.096
37	1.0002	0.872	0.336	5.275	0.933	9015	0.590	0.455	0.001	-0.344	1.216	0.112
38	1.0010	1.900	0.141	5.275	0.392	9974	0.652	0.455	0.001	0.260	1.640	0.124
39	1.0014	2.663	0.127	5.350	0.362	11779	0.781	0.379	0.001	0.418	2.246	0.146
40	1.0034	2.222	0.209	5.350	0.595	13220	0.877	0.378	0.001	0.286	1.942	0.164

Table E-2 (continued). Data and Calculations for Determining Desorption Isotherms for Naphthalene and California Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)												
Sample	M _s (gm)	Γ (μgm/gm)	C _e (mg/L)	V _s + V _n (mL)	M _{n i} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _n (mL)	M _n (μgm)	M _d (μ/gm)	Γ (μgm/gm)	C _s (mg/L)
1.00% Surfactant added												
41	1.0033	0.396	0.029	5.050	0.074	2460	0.154	0.679	0.000	0.079	0.316	0.031
42	1.0009	0.397	0.029	5.050	0.074	2421	0.152	0.680	0.000	0.077	0.319	0.030
43	1.0091	0.921	0.065	5.125	0.170	5370	0.341	0.601	0.001	0.169	0.753	0.067
44	1.0028	0.464	0.155	5.125	0.408	4077	0.259	0.604	0.000	-0.149	0.613	0.051
45	1.0009	1.582	0.079	5.200	0.213	8512	0.549	0.530	0.001	0.334	1.248	0.106
46	1.0044	1.396	0.114	5.200	0.307	8332	0.537	0.528	0.001	0.228	1.166	0.103
47	1.0012	1.680	0.183	5.275	0.507	11185	0.732	0.454	0.001	0.223	1.457	0.139
48	1.0016	1.172	0.279	5.275	0.774	9068	0.593	0.454	0.001	-0.181	1.353	0.112
49	1.0045	2.432	0.169	5.350	0.481	14395	0.955	0.378	0.001	0.470	1.962	0.178
50	1.0078	1.609	0.322	5.350	0.918	11776	0.781	0.376	0.001	-0.137	1.746	0.146

Table E-3. Data and Calculations for Determining Desorption Isotherms for Naphthalene and Greenville Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)												
Sample	M _s (gm)	Γ (μgm/gm)	C _e (mg/L)	V _s + V _n (mL)	M _{n i} (μgm)	DPH/mL (DPH/mL)	M _n (μgm)	V _s (mL)	M _s (μgm)	M _d (μ/gm)	Γ (μgm/gm)	C _e (mg/L)
<u>No Surfactant added</u>												
1	1.0031	0.149	0.077	5.050	0.196	3474	0.218	0.638	0.000	0.021	0.127	0.043
2	1.0006	0.089	0.089	5.050	0.226	4105	0.257	0.640	0.000	0.030	0.059	0.051
3	1.0052	0.199	0.208	5.125	0.546	9573	0.608	0.562	0.001	0.061	0.138	0.119
4	1.0013	0.204	0.207	5.125	0.544	9504	0.604	0.564	0.001	0.058	0.145	0.118
5	1.0043	0.343	0.317	5.200	0.857	14757	0.951	0.488	0.001	0.093	0.250	0.183
6	1.0009	0.297	0.326	5.200	0.881	15135	0.976	0.490	0.001	0.093	0.204	0.188
7	1.0042	0.352	0.431	5.275	1.196	20387	1.333	0.413	0.002	0.136	0.216	0.253
8	1.0024	0.335	0.434	5.275	1.205	20572	1.345	0.414	0.002	0.139	0.196	0.255
9	1.0088	0.540	0.530	5.350	1.509	25325	1.680	0.336	0.002	0.167	0.373	0.314
10	1.0027	0.401	0.556	5.350	1.585	25665	1.702	0.339	0.002	0.115	0.286	0.318
<u>0.01% Surfactant added</u>												
11	1.0070	0.069	0.093	5.050	0.236	4271	0.267	0.637	0.001	0.031	0.038	0.053
12	1.0035	0.082	0.090	5.050	0.230	4234	0.265	0.638	0.001	0.035	0.047	0.052
13	1.0012	0.176	0.213	5.125	0.558	9714	0.617	0.564	0.001	0.058	0.119	0.120
14	1.0043	0.218	0.204	5.125	0.536	9694	0.616	0.563	0.001	0.076	0.140	0.120
15	1.0095	0.324	0.321	5.200	0.866	15360	0.990	0.485	0.001	0.122	0.202	0.190
16	1.0033	0.333	0.319	5.200	0.862	15162	0.978	0.486	0.001	0.114	0.219	0.188
17	1.0030	0.343	0.432	5.275	1.200	20633	1.349	0.414	0.002	0.147	0.196	0.256
18	1.0046	0.392	0.423	5.275	1.174	20258	1.325	0.413	0.002	0.149	0.244	0.251
19	1.0025	0.545	0.529	5.350	1.508	26400	1.751	0.339	0.002	0.241	0.305	0.327
20	1.0027	0.495	0.539	5.350	1.535	26310	1.745	0.339	0.002	0.208	0.287	0.326

Table E-3 (continued). Data and Calculations for Determining Desorption Isotherms for Naphthalene and Greenville Soil Using Five Different Surfactant Concentrations

(From Adsorption Data)											
Sample	M_s (gm)	Γ ($\mu\text{gm/gm}$)	C_e (mg/L)	$V_s + V_n$ (mL)	M_{n1} (μgm)	DPH/mL (DPH/mL)	M_n (μgm)	V_n (mL)	M_n (μgm)	H_d ($\mu\text{gm/gm}$)	C_d (mg/L)
0.05% Surfactant added											
21	1.0013	0.064	0.094	5.050	0.239	4440	0.278	0.639	0.001	0.039	0.055
22	1.0094	0.087	0.089	5.050	0.227	4034	0.253	0.635	0.000	0.025	0.050
23	1.0017	0.209	0.206	5.125	0.541	9420	0.599	0.554	0.001	0.056	0.117
24	1.0071	0.208	0.206	5.125	0.542	9637	0.612	0.562	0.001	0.069	0.119
25	1.0074	0.278	0.330	5.200	0.890	14930	0.963	0.486	0.001	0.071	0.185
26	1.0067	0.304	0.325	5.200	0.877	14874	0.959	0.487	0.001	0.081	0.184
27	1.0032	0.384	0.425	5.275	1.179	19617	1.283	0.413	0.002	0.103	0.243
28	1.0033	0.330	0.435	5.275	1.207	19982	1.307	0.413	0.002	0.096	0.248
29	1.0010	0.488	0.540	5.350	1.540	24816	1.646	0.340	0.002	0.105	0.308
30	1.0083	0.477	0.541	5.350	1.543	24913	1.653	0.336	0.002	0.107	0.309
0.25% Surfactant added											
31	1.0059	0.082	0.090	5.050	0.229	3113	0.195	0.637	0.000	-0.035	0.039
32	1.0081	0.089	0.089	5.050	0.226	3063	0.192	0.636	0.000	-0.034	0.038
33	1.0051	0.246	0.199	5.125	0.522	7200	0.458	0.563	0.001	-0.065	0.089
34	1.0042	0.177	0.212	5.125	0.538	6940	0.441	0.563	0.001	-0.117	0.086
35	1.0069	0.368	0.312	5.200	0.643	11467	0.739	0.487	0.001	-0.104	0.142
36	1.0015	0.310	0.324	5.200	0.874	11083	0.715	0.489	0.001	-0.161	0.137
37	1.0068	0.331	0.435	5.275	1.206	14332	0.937	0.412	0.001	-0.268	0.178
38	1.0054	0.369	0.427	5.275	1.186	14814	0.969	0.412	0.001	-0.217	0.184
39	1.0064	0.436	0.549	5.350	1.566	18576	1.232	0.337	0.001	-0.333	0.230
40	1.0072	0.511	0.535	5.350	1.526	18508	1.228	0.336	0.001	-0.297	0.229

Table E-3 (continued). Data and Calculations for Determining Desorption Isotherms for Naphthalene on Greenville Soils Using Five Different Surfactant Concentrations

Sample	(From Adsorption Data)										
	M_s (gm)	Γ ($\mu\text{gm/gm}$)	C_s (mg/L)	$V_s + V_h$ (mL)	M_h (μgm)	DPH/mL (DPH/mL)	M_h (μgm)	V_h (mL)	M_h (μgm)	Γ ($\mu\text{gm/gm}$)	C_s (mg/L)
1.00% Surfactant added											
41	1.0014	0.067	0.093	5.050	0.237	1652	0.103	0.639	0.000	-0.134	0.020
42	1.0006	0.266	0.054	5.050	0.137	*	*	*	*	*	*
43	1.0060	0.204	0.207	5.125	0.544	3718	0.236	0.562	0.000	-0.306	0.046
44	1.0088	0.210	0.206	5.125	0.540	3645	0.232	0.561	0.000	-0.307	0.045
45	1.0017	0.343	0.317	5.200	0.857	5652	0.364	0.489	0.001	-0.492	0.070
46	1.0064	0.298	0.326	5.200	0.880	5597	0.361	0.487	0.001	-0.516	0.069
47	1.0012	0.380	0.426	5.275	1.181	7841	0.513	0.414	0.001	-0.668	0.097
48	1.0056	0.356	0.430	5.275	1.193	7757	0.507	0.412	0.001	-0.682	0.096
49	1.0041	0.574	0.524	5.350	1.492	9993	0.663	0.338	0.001	-0.827	0.124
50	1.0018	0.506	0.537	5.350	1.530	9668	0.641	0.339	0.001	-0.887	0.120

Table E.4 Values of pH and Specific Conductance for Naphthalene Equilibrium Sorption Studies for Charleston, California and Greenville soils

Samp.	Surfactant Concentration Added (%)	Charleston Soil		California Soil		Greenville Soil	
		pH	Specific ^a Conductance ($\mu\text{mho/cm}$)	pH	Specific ^a Conductance ($\mu\text{mho/cm}$)	pH	Specific ^a Conductance ($\mu\text{mho/cm}$)
A	0.00	4.68	8.40	6.58	9.20	5.06	8.35
B	0.01	4.66	8.60	6.75	9.35	4.90	6.00
C	0.05	4.65	9.00	6.56	9.40	5.03	6.55
D	0.25	4.64	9.00	6.44	10.00	5.01	7.20
E	1.00	4.64	8.90	6.35	11.00	5.36	9.70

^aspecific conductance for a 10:1 dilution of the sample

Appendix FData for Column Runs

This appendix contains the data and calculations for the normalized concentration versus pore volume curves and the cumulative normalized mass eluted curves for the column studies.

Table F-1. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 1, and Elution Rate = 20 mL/hr (Water Wash)

Naphthalene Loading				Naphthalene Elution			
Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Under Effluent Concentration Naphthalene vs. PV curve
0.0	0.00	0.000		0.0	7.15	0.942	0.000
4.1	0.01	0.001	31.1	8.3	5.49	0.723	52.456
16.3	0.03	0.004	123.5	13.7	5.06	0.667	80.941
33.4	0.37	0.049	249.8	19.3	4.30	0.557	107.149
38.2	0.86	0.113	283.3	22.0	3.89	0.513	118.206
42.5	1.54	0.203	310.8	29.3	2.70	0.356	142.259
47.4	2.64	0.348	337.7	33.1	2.38	0.314	151.911
52.5	3.63	0.478	360.4	37.0	1.87	0.246	160.199
59.0	4.92	0.648	382.0	39.8	1.58	0.208	165.029
66.3	6.00	0.791	397.5	43.4	1.02	0.134	169.709
72.4	6.71	0.884	405.1	49.9	0.69	0.091	175.266
80.1	7.04	0.928	410.6	54.2	0.61	0.080	178.061
88.6	7.54	0.993	413.1	57.2	0.36	0.047	179.516
104.9	7.31	0.963	415.8	61.3	0.22	0.029	180.705
114.7	6.78	0.893	421.2	70.4	0.07	0.009	182.025
121.4	6.96	0.917	426.0	81.2	0.06	0.008	182.727
126.9	7.15	0.942	428.9	91.5	0.08	0.011	183.448

$C_0 = 7.59 \text{ mg/L}$
 $Q = 0.96 \pm 0.02$
 $\theta = 0.13 \pm 0.02$
 $\tau = 52.43 \pm 1.10$

Table F-2. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 2, and Elution Rate = 20 mL/hr (Surfactant Wash)

Naphthalene Loading				Naphthalene Elution				
Pore Volumes (mg/L)	Effluent Concentration	Normalized Effluent Concentration	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes (mg/L)	Effluent Concentration	Normalized Effluent Concentration	Area Under Effluent Concentration Naphthalene vs. PV curve	Influent Pressure (psi)
0.0	0.00	0.000		0.0	6.57	0.882		0.000
4.0	0.01	0.001	29.8	8.3	6.65	0.893	54.863	0.128
15.8	0.02	0.003	117.5	13.7	5.99	0.804	88.991	0.207
32.4	0.81	0.109	234.3	19.3	6.87	0.922	124.999	0.291
37.1	1.46	0.196	264.0	22.0	7.85	1.054	144.871	0.338
41.3	2.14	0.287	287.7	29.3	8.06	1.082	202.943	0.473
46.0	3.01	0.404	310.6	33.1	8.05	1.081	233.552	0.544
51.0	3.79	0.509	330.9	37.0	6.70	0.899	262.314	0.612
57.3	4.72	0.634	351.0	39.8	5.08	0.682	278.806	0.650
64.4	5.27	0.707	368.4	43.4	3.78	0.507	294.754	0.687
70.3	5.94	0.797	379.3	49.9	1.59	0.213	312.207	0.728
77.8	6.22	0.835	389.6	54.2	1.78	0.239	319.452	0.745
86.1	6.89	0.925	397.0	57.2	0.51	0.068	322.887	0.753
102.4	6.44	0.864	409.8	61.3	0.35	0.047	324.650	0.757
112.1	6.30	0.846	420.3	70.4	0.21	0.028	327.198	0.763
118.8	6.44	0.864	427.5	81.2	0.18	0.024	329.304	0.768
124.3	6.57	0.882	432.7	91.5	0.08	0.011	330.643	0.771

$C_0 = 7.45 \text{ mg/L}$

$\sigma = 0.87 \pm 0.02$

$\theta = 0.11 \pm 0.02$

$\tau = 48.26 \pm 1.24$

Table F-3. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 1, and Elution Rate = 40 mL/hr (Water Wash)

Naphthalene Loading				Naphthalene Elution			
Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene vs. PV curve	Area Under Effluent Concentration Naphthalene vs. PV curve
0.0	0.00	0.000		0.0	5.19	0.899	0.000
25.3	1.09	0.189	132.2	1.9	4.78	0.828	9.472
28.9	1.55	0.269	148.2	3.8	4.79	0.830	18.563
32.5	2.32	0.403	162.0	8.6	4.64	0.804	41.195
37.4	2.68	0.464	178.0	13.6	3.63	0.629	62.697
41.0	3.22	0.558	188.2	20.0	2.58	0.447	81.948
44.6	3.62	0.627	196.6	24.0	1.82	0.315	90.748
50.6	4.14	0.718	208.0	30.6	1.34	0.232	101.176
54.8	4.22	0.731	214.7	35.5	1.05	0.182	107.032
59.0	4.50	0.780	220.6	38.9	0.88	0.153	110.313
62.7	4.76	0.825	224.8	43.7	0.48	0.083	113.577
81.9	4.89	0.847	242.9	56.7	0.12	0.021	117.477
90.4	5.14	0.891	249.4				
97.6	5.20	0.901	253.7				
113.3	5.19	0.899	262.7				

$C_0 = 5.77$ mg/L

$Q = 0.88 \pm 0.02$

$\theta = 0.10 \pm 0.01$

$\tau = 36.23 \pm 1.25$

Table F-4. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 2, and Elution Rate = 40 mL/hr (Surfactant Wash)

Naphthalene Loading				Naphthalene Elution				
Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Under Effluent Concentration Naphthalene vs. PV curve	Influent Pressure (psi)
0.0	0.00	0.000		0.0	4.58	0.821		0.000
25.3	1.28	0.229	125.0	2.3	4.60	0.824	10.557	0.037
28.9	1.53	0.274	140.0	4.5	4.72	0.846	20.809	0.073
32.5	1.95	0.349	153.8	10.3	4.00	0.717	46.037	0.162
37.4	2.15	0.385	171.1	16.5	3.23	0.579	68.510	0.240
41.0	2.65	0.475	182.6	23.9	4.01	0.719	95.298	0.334
44.6	3.10	0.556	192.3	28.8	4.23	0.758	115.486	0.405
50.6	3.42	0.613	206.2	36.7	3.51	0.629	146.059	0.513
54.8	3.76	0.674	214.6	42.5	2.95	0.529	164.793	0.578
59.0	3.91	0.701	221.9	46.6	2.28	0.409	175.515	0.616
62.7	4.09	0.733	227.8	52.4	1.23	0.220	185.694	0.652
81.9	4.30	0.771	254.4	67.9	0.00	0.000	195.226	0.685
90.4	4.57	0.819	264.1					
97.6	4.76	0.853	270.7					
113.3	4.58	0.821	285.0					

$C_0 = 5.58$ mg/L

$\sigma = 0.82 \pm 0.02$

$\theta = 0.08 \pm 0.01$

$\tau = 37.10 \pm 1.42$

Table F-5. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 1, and Elution Rate = 60 mL/hr (Water Wash)

Naphthalene Loading				Naphthalene Elution			
Pore Volumes (mg/L)	Effluent Concentration Naphthalene	Normalized Effluent Concentration Naphthalene	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes (mg/L)	Effluent Concentration Naphthalene	Normalized Effluent Concentration Naphthalene	Area Under Effluent Concentration Naphthalene vs. PV curve
0.0	0.00	0.000		0.0	4.80	0.870	0.000
22.6	0.00	0.000	124.8	4.5	4.67	0.846	0.067
28.9	0.00	0.000	159.5	8.7	3.81	0.690	0.124
37.7	0.58	0.105	205.6	13.6	3.31	0.600	0.179
41.6	1.88	0.341	222.3	17.6	2.79	0.505	0.217
44.4	2.62	0.475	231.4	21.0	2.46	0.446	0.246
46.9	3.35	0.607	237.6	26.1	2.09	0.379	0.282
50.2	3.42	0.620	244.8	31.2	1.82	0.330	0.314
52.9	3.76	0.681	250.0	40.2	1.28	0.232	0.358
55.4	3.91	0.708	254.2	45.3	1.16	0.210	0.378
71.1	4.23	0.766	277.0	49.7	0.98	0.178	0.392
87.2	4.73	0.857	293.8	56.7	0.59	0.107	0.410
97.1	4.67	0.846	301.9	87.3	0.16	0.029	0.446
105.4	4.69	0.850	308.8				
115.0	4.80	0.870	316.3				

$C_0 = 5.52$ mg/L

$Q = 0.82 \pm 0.04$

$\theta = 0.21 \pm 0.06$

$\tau = 43.76 \pm 1.33$

Table F-6. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 2, and Elution Rate = 60 mL/hr (Surfactant Wash)

Naphthalene Loading				Naphthalene Elution				
Pore Volumes (mg/L)	Effluent Concentration	Normalized Effluent Concentration	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes (mg/L)	Effluent Concentration	Normalized Effluent Concentration Naphthalene vs. PV curve	Area Under Effluent Concentration Naphthalene vs. PV curve	Influent Pressure (psi)
0.0	0.00	0.000		0.0	5.23	0.908		0.000
20.8	0.01	0.002	119.7	4.9	4.96	0.861	24.966	0.088
26.6	0.02	0.003	153.0	9.5	3.79	0.658	45.091	0.159
34.7	1.12	0.194	195.1	14.8	3.85	0.668	65.337	0.230
38.3	2.33	0.405	209.6	19.2	4.19	0.727	83.025	0.292
40.8	3.20	0.556	217.1	22.9	4.46	0.774	99.027	0.349
43.1	3.91	0.679	222.1	28.5	4.86	0.844	125.123	0.440
46.2	5.99	0.893	227.8	34.1	4.73	0.821	151.975	0.535
48.7	4.10	0.712	232.0	43.8	2.47	0.429	186.895	0.658
51.0	4.29	0.745	235.6	49.4	1.46	0.253	197.899	0.697
65.4	4.76	0.826	253.4	54.2	0.59	0.102	202.819	0.714
80.3	4.79	0.832	268.1	61.9	0.39	0.068	206.592	0.727
89.3	5.14	0.892	275.3	95.2	0.16	0.028	215.750	0.759
97.0	5.21	0.905	279.8					33.0
105.9	5.33	0.925	284.1					

$C_0 = 5.76$ mg/L

$\sigma = 0.86 \pm 0.05$

$\theta = 0.23 \pm 0.07$

$\tau = 38.99 \pm 1.26$

Table F-7. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 1, and Elution Rate = 90 mL/hr (Water Wash)

Naphthalene Loading				Naphthalene Elution			
Pore Volumes (mg/L)	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes (mg/L)	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene	Area Under Effluent Concentration Naphthalene vs. PV curve
0.0	0.00	0.000		0.0	6.81	0.912	0.000
24.3	0.21	0.028	179.0	0.9	6.36	0.851	0.016
29.2	0.72	0.096	213.3	4.7	6.11	0.818	5.927
34.0	1.54	0.206	243.7	8.5	5.70	0.763	29.620
40.1	2.75	0.368	276.2	12.2	5.16	0.691	52.059
42.1	4.04	0.541	284.4	18.8	3.93	0.526	72.150
45.0	4.77	0.639	293.2	26.9	2.96	0.396	102.147
49.0	5.34	0.715	302.9	30.7	2.62	0.351	130.051
53.9	5.72	0.766	312.4	36.0	2.23	0.299	140.653
58.7	5.89	0.788	320.4	43.5	1.88	0.252	153.506
78.2	6.21	0.831	348.1	52.9	1.50	0.201	166.918
83.8	6.50	0.870	354.3	62.3	1.30	0.174	184.804
89.7	6.57	0.880	359.9	78.9	0.95	0.127	197.964
100.5	6.86	0.918	368.0	97.7	0.70	0.094	216.639
				148.4	0.24	0.032	232.149
							255.978
							0.696

$C_0 = 7.47$ mg/L

$Q = 0.86 \pm 0.03$

$\theta = 0.19 \pm 0.04$

$\tau = 40.37 \pm 1.15$

Table F-8. Data for Plotting Normalized Naphthalene Loading Curve, Normalized Naphthalene Elution Curve, and Normalized-Cumulative Mass Naphthalene Eluted Curve for Column Number 2, and Elution Rate = 90 mL/hr (Surfactant Wash)

Naphthalene Loading				Naphthalene Elution				
Pore Volumes	Effluent Concentration (mg/L)	Normalized Effluent Concentration Naphthalene vs. PV curve	Area Between C_0 & Effluent Concentration Naphthalene vs. PV curve	Pore Volumes	Effluent Concentration Naphthalene (mg/L)	Normalized Effluent Concentration Naphthalene vs. PV curve	Area Under Effluent Concentration Naphthalene vs. PV curve	Influent Pressure (psi)
0.0	0.00	0.000		0.0	5.98	0.886		0.000
23.8	0.06	0.009	159.9	6.9	5.91	0.876	5.351	0.017
28.6	0.19	0.028	191.7	4.7	6.05	0.896	28.075	0.087
33.3	0.62	0.092	221.6	8.5	5.33	0.790	49.697	0.155
39.3	2.01	0.298	254.2	12.6	4.18	0.619	69.192	0.215
41.3	3.77	0.559	261.9	21.1	4.95	0.733	107.995	0.336
44.0	4.46	0.661	269.0	31.5	5.20	0.770	160.775	0.500
46.0	5.20	0.770	276.7	36.5	4.91	0.727	186.050	0.579
52.8	5.57	0.825	283.2	42.9	4.23	0.627	215.298	0.670
57.5	5.85	0.867	288.1	51.8	2.90	0.430	247.026	0.768
76.6	5.83	0.864	305.5	63.0	1.19	0.176	269.930	0.840
82.1	6.00	0.889	310.1	74.2	0.71	0.105	280.570	0.873
87.9	6.11	0.905	314.1	93.9	0.14	0.021	286.943	0.899
98.4	5.98	0.886	321.5					45.0

$C_0 = 6.75$ mg/L

$Q = 0.87 \pm 0.01$

$\theta = 0.31 \pm 0.03$

$\tau = 40.45 \pm 0.70$

Appendix G

Modeled Elution Data

This appendix contains plots of data and fitted models for the normalized concentration versus pore volume curves and the cumulative normalized mass eluted curves prepared for the column studies.

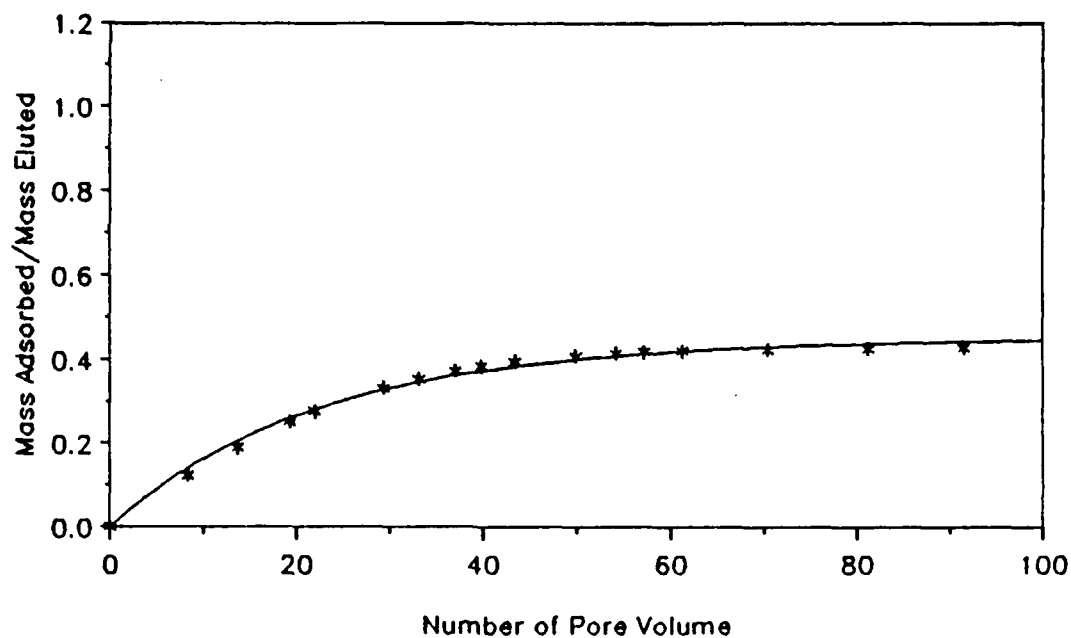


Figure G-1. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Water at a Flow Rate of 20 mL/h

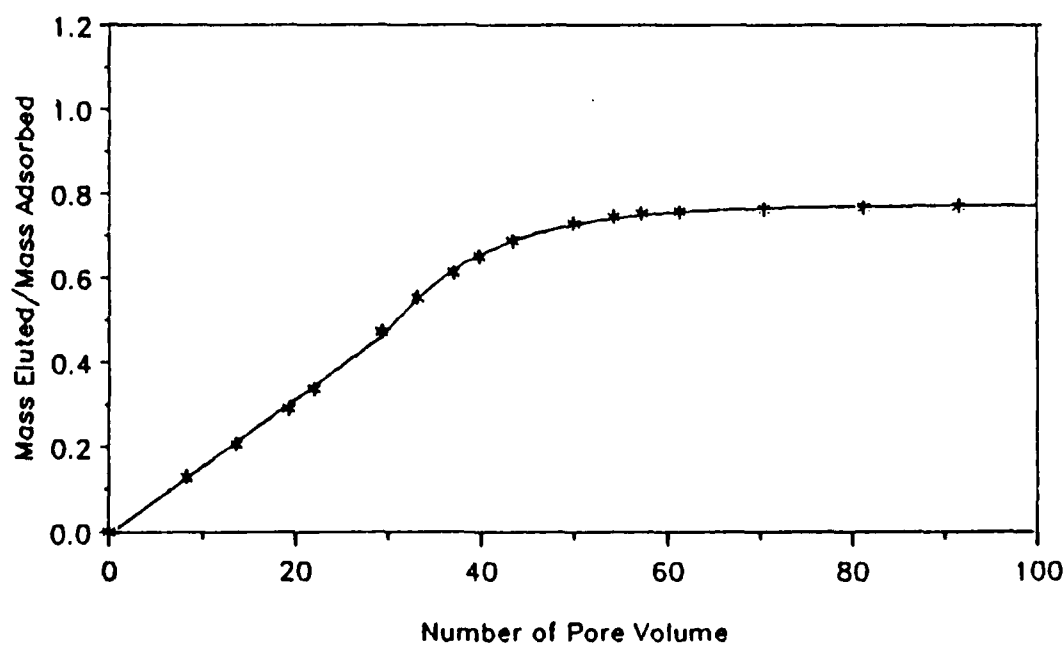


Figure G-2. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Surfactant Solution at a Flow Rate of 20 mL/h

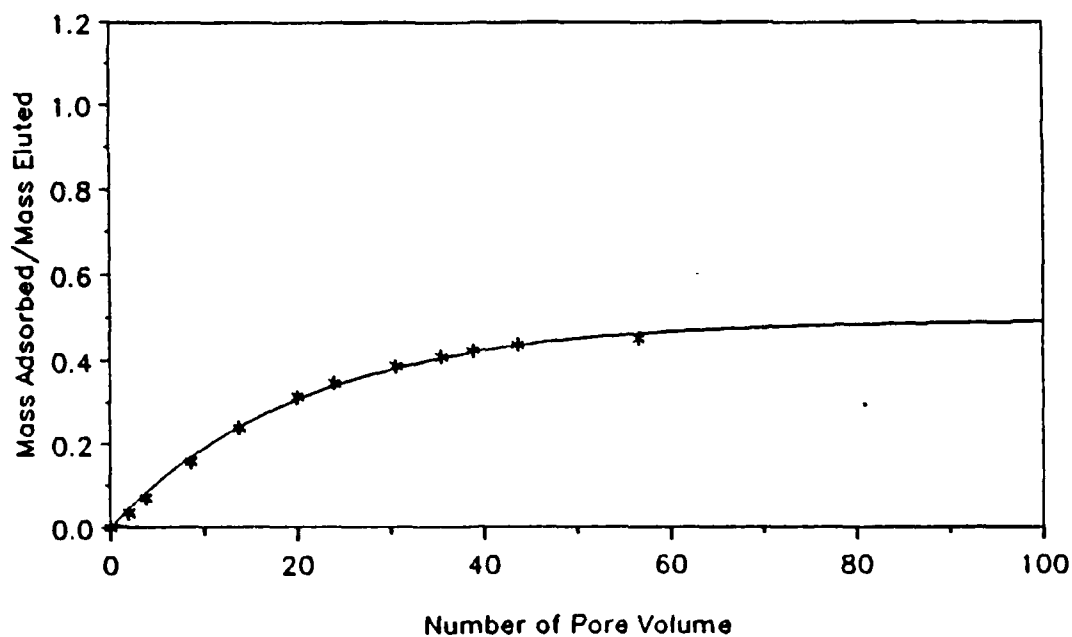


Figure G-3. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Water at a Flow Rate of 40 mL/h

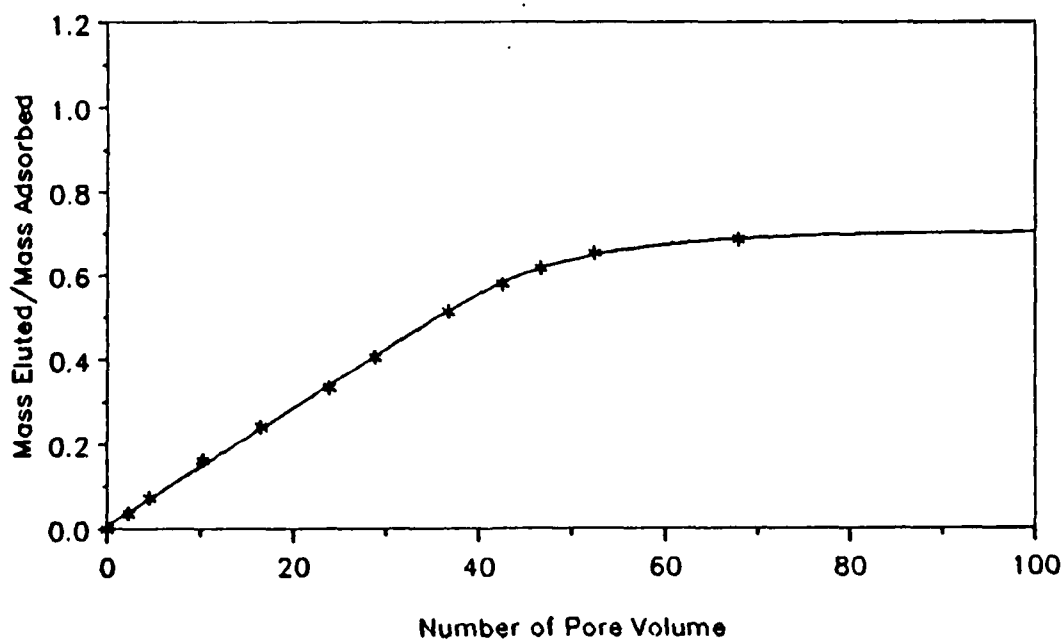


Figure G-4. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Surfactant Solution at a Flow Rate of 40 mL/h

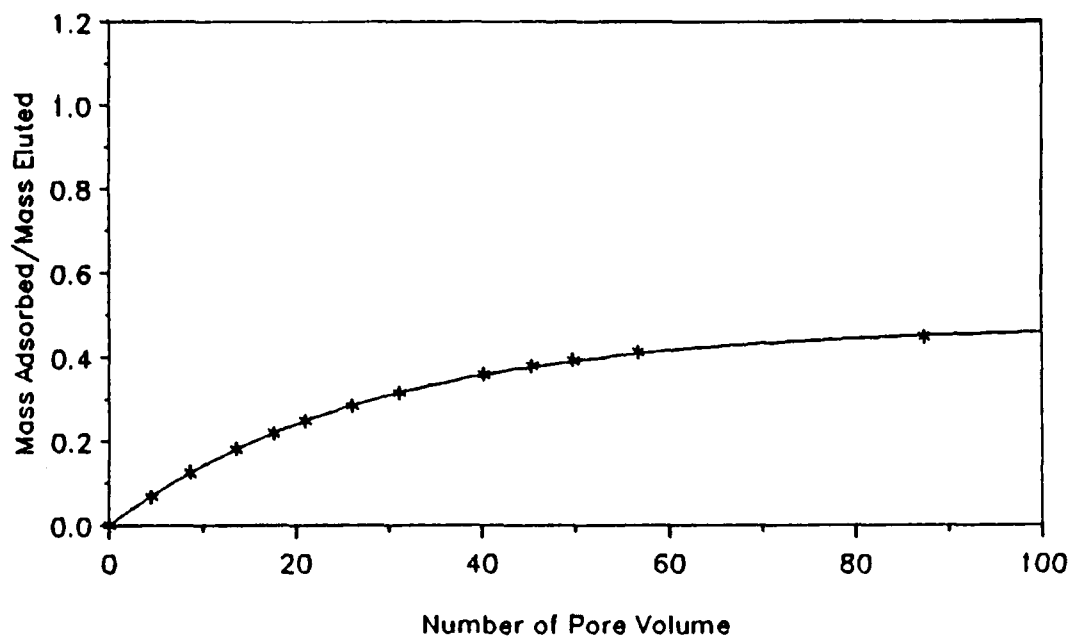


Figure G-5. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Water at a Flow Rate of 60 mL/h

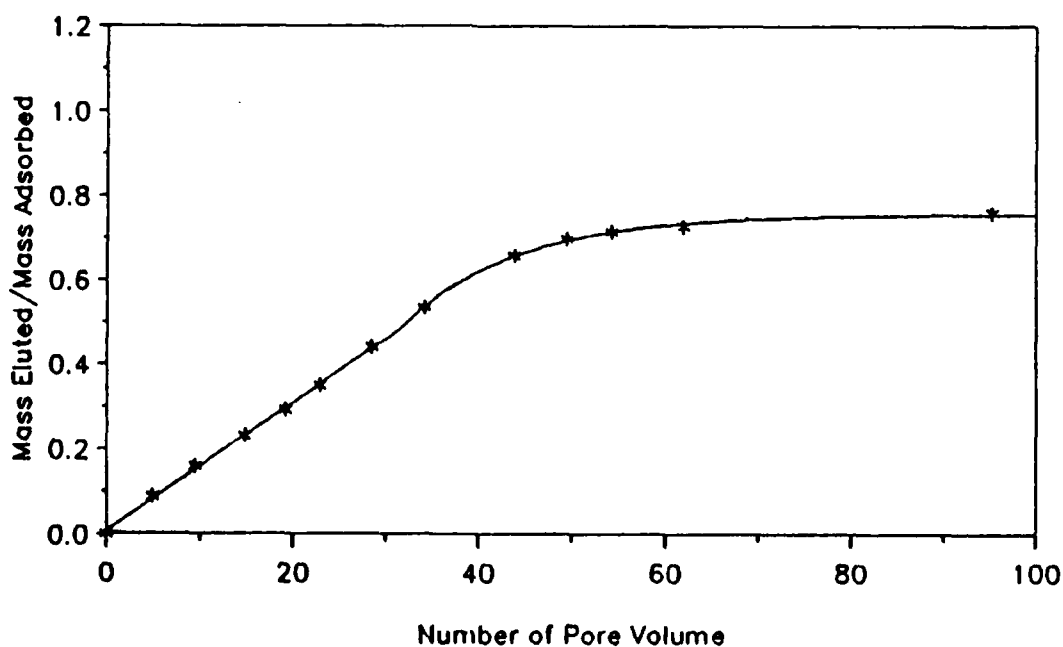


Figure G-6. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Surfactant Solution at a Flow Rate of 60 mL/h

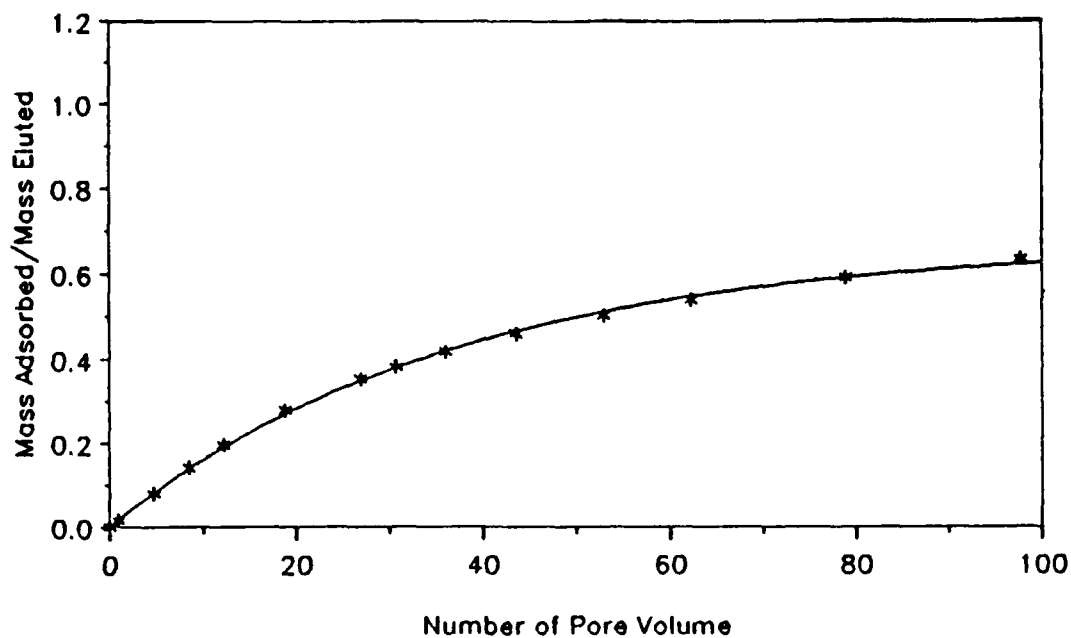


Figure G-7. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Water at a Flow Rate of 90 mL/h

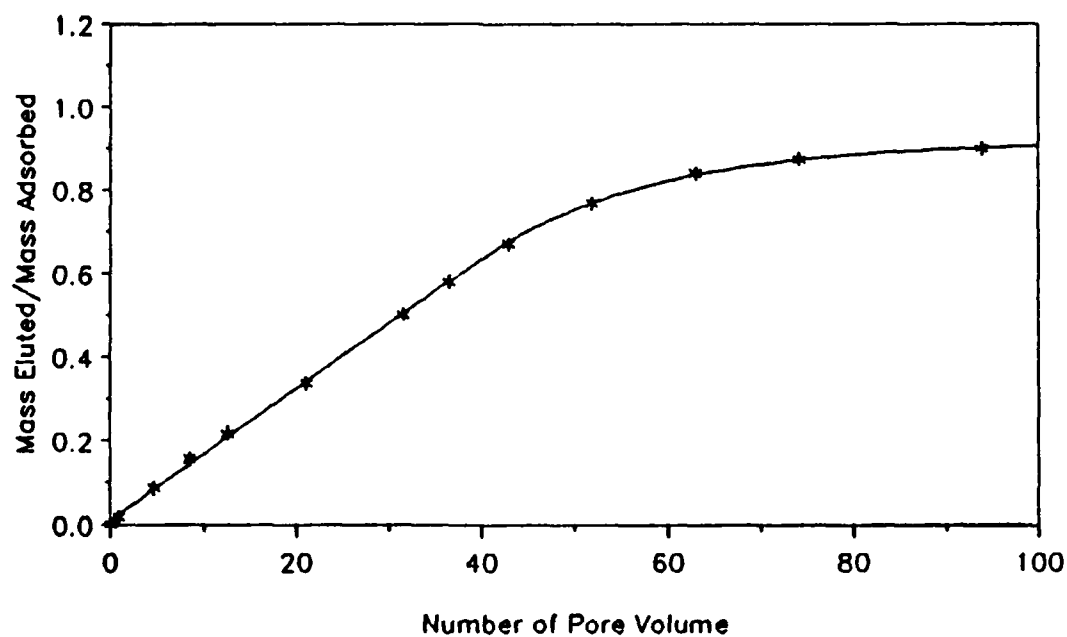


Figure G-8. Fitted Model and Data Points for Cumulative Mass Naphthalene Eluted with Surfactant Solution at a Flow Rate of 90 mL/h

LIST OF SYMBOLS

A	parameter relating CMC's to alkyl chain lengths (unitless)
α	statistical parameter representing the soil equilibrium adsorption capacity in kinetic experiments ($\mu\text{g/g}$)
α'	statistical parameter representing the soil equilibrium desorption capacity in kinetic experiments ($\mu\text{g/g}$)
α_1	statistical parameter representing the vertical axis intercept of the linear portion of the surface tension vs. log percent surfactant concentration at surfactant concentrations below the CMC (dynes/cm)
α_2	statistical parameter representing the vertical axis intercept of the linear portion of the surface tension vs. log percent surfactant concentration at surfactant concentrations above the CMC (dynes/cm)
B	parameter relating CMC's to alkyl chain lengths (unitless)
β	statistical parameter related to the rate at which the system attains equilibrium in adsorption kinetic experiments (hrs^{-1})
β'	statistical parameter related to the rate at which the system attains equilibrium in desorption kinetic experiments (hrs^{-1})
β_1	statistical parameter representing the slope of the linear portion of the the surface tension vs. log percent surfactant concentration curve at surfactant concentrations below the CMC (unitless)
β_2	statistical parameter representing the slope of the linear portion of the the surface tension vs. log percent surfactant concentration curve at surfactant concentrations above the CMC (unitless)
$C(x,t)$	aqueous solute concentration referenced to position and time ($\text{kg solute/m}^3 \text{ water}$)
C_{adjusted}	naphthalene concentration adjusted for surfactant interference (mg/L)
C_{cs}	concentration of clay particles (mg/L)
C_e	equilibrium solution concentration of naphthalene ($\mu\text{g/L}$)
$(C_e)_{\text{ads}}$	equilibrium solution concentration of naphthalene after the adsorption phase of the equilibrium sorption studies ($\mu\text{g/L}$)

CMC	critical micelle concentration (%)
C _o	Average naphthalene concentration of influent to column (mg/L), or for kinetic experiments, the concentration of the compound in solution prior to diluting to initiate the desorption experiment (µg/L)
C _{read}	naphthalene concentration not adjusted for surfactant interference (mg/L)
C _s	concentration of surfactant (%)
C _{sb}	concentration of surfactant in surfactant blank (%)
C _{sf}	total concentration of surfactant (mol/L)
CSSE	sum of squares error for the conditioned model (unitless)
C _t	solution concentration of compound in reactor (µg/L)
C _{to}	total concentration of the compound in the vial at the outset of the desorption experiment (µg/L)
d	particle diameter (m)
df	degrees of freedom (unitless)
D	diameter of column (cm)
D _{ab}	diffusivity of compound a in b (cm ² /s)
D _t	dispersivity (m ² /day)
δ	partial differential operator (unitless)
ε	statistical parameter representing the surface tension at the CMC (dynes/cm)
ε ₁₁ -ε ₄	statistical parameters in model for cumulative normalized elution curves (unitless)
f	fraction of the volume of solution remaining after a portion of the solution was removed to dilute each batch reactor prior to initiating the desorption experiment (unitless)
f _{oc}	fraction organic content (unitless)
φ	statistical parameter related to naphthalene dispersion within the column (unitless)
φ _r	shape factor (unitless)
Φ	statistical parameter representing the log percent surfactant at the CMC (unitless)
Γ	mass naphthalene adsorbed per gram soil (µg/g)

Γ'	mass naphthalene desorbed per gram soil ($\mu\text{g/g}$)
Γ_{ads}	mass naphthalene adsorbed per gram soil ($\mu\text{g/g}$)
Γ_{des}	mass naphthalene desorbed per gram soil ($\mu\text{g/g}$)
Γ_{max}	ultimate compound sorption capacity of the sorbent ($\mu\text{g/g}$)
Γ_r	soil phase concentration of solute as a function of the radial dimension, r ($\mu\text{g/g}$)
I	Ionic strength (unitless)
k_a	adsorption rate constant ($\text{L}/\mu\text{g}\cdot\text{h}$)
k_d	desorption rate constant ($/\text{h}$)
K_f	mass transfer coefficient (cm/s)
K_d	partition coefficient of solute between solid and aqueous phase ($\mu\text{g/g}$)
K_d'	partition coefficient of solute between solid and aqueous phase referenced particularly to the desorption phase of the equilibrium experiments ($\mu\text{g/g}$)
K_{oc}	partition coefficient of solute between solid and aqueous phase referenced to organic carbon content ($\mu\text{g/g}$)
K_m	partition coefficient of solute between micellar and aqueous phase (mole fraction)
K_1	empirical constant relating M_1 and m_2 (unitless)
L	depth of soil in the column (cm)
m_1	concentration of surfactant ions (mol/L)
m_2	concentration of counter ions (mol/L)
M_a	mass of naphthalene adsorbed to soil in column (mg)
M_e	mass of naphthalene eluted from column (mg)
M_d	mass of naphthalene desorbed (μg)
M_g	mass of naphthalene in gas phase (μ)
M_n	mass of naphthalene in solution (μg)
M_{n1}	mass of naphthalene in solution at outset of desorption experiment (μg)
M_{nt}	total mass of naphthalene in vial at outset of adsorption experiment (μg)

M_s	mass of soil (g)
μ	dynamic viscosity of water (N·s/m ²)
n	soil porosity (m ³ /m ³)
n_o	number of observations (unitless)
n_1	alkyl chain length of surfactant (unitless)
N	number of pore volumes (unitless)
NR_e	Reynolds number (unitless)
OC	organic content (unitless)
Ω	statistical parameter representing the maximum concentration of naphthalene eluted from the column after breakthrough (mg/L)
p	number of parameters in a statistical model
p_v	pore volume (mL)
$PCDE$	percent clay dispersion effect (unitless)
Q	flow rate through column (mL/h)
r	rank, or number of parametric restrictions associated with a hypothesis (unitless)
R	retardation factor (unitless)
$S(x,t)$	sorbed solute concentration referenced to position and time (kg solute/kg soil)
Sc	Schmidt number (unitless)
S_{es}	spectrophotometer reading at wavelengths 278/565 nm on the sample from column with surfactant wash (unitless)
S_{ew}	spectrophotometer reading at wavelengths 278/565 nm on the sample from column with water wash (unitless)
SSH	sum of squares of the hypothesis (unitless)
SSE	sum of squares error (unitless)
S_v	specific volume of soil (mL/g)
σ	density of water (kg/m ³)
σ_b	soil bulk density (kg soil/m ³ bulk volume)
Σ	statistical parameter used in model for cumulative normalized elution curves (unitless)

t	time (hr or day)
T	absolute temperature($^{\circ}$ K)
T _{.95}	time required to attain 95 percent of soil's equilibrium sorption capacity (h)
τ	statistical parameter representing the inflection point of the naphthalene breakthrough curve (pv)
θ	liquid solid contact angle (degrees)
v _b	molar volume of solute at its boiling point (m ³ /mol)
v _t	average flow velocity (m/day)
v _w	molar volume of water (L/mol)
V	interstitial velocity (m/s)
V _a	volume of air (mL)
V _e	volume eluted from column (mL)
V _n	volume of naphthalene stock solution (mL)
V _s	volume of soil (mL)
V _t	total volume of additives (mL)
V _w	volume of water (mL)
x	spatial coordinate (m)
X	log percent surfactant concentration (unitless)
Y	surface tension (dynes/cm)
Z	statistical parameter that is set to zero if data point is below the intersection of two functions, and 1 if the data point is above the intersection (unitless)
Z ₁	statistical parameter that is set to zero if sorption data is from the desorption experiment, and 1 if data is from the adsorption experiment (unitless)

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